2010

Laboratory Studies To Field Evaluation : Remediation Of Polychlorinated Biphenyl Contaminated Painted Surfaces Through The Use Of Activated Metal Treatment Systems

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LABORATORY STUDIES TO FIELD EVALUATION; REMEDIATION OF POLYCHLORINATED BIPHENYL CONTAMINATED PAINTED SURFACES THROUGH THE USE OF ACTIVATED METAL TREATMENT SYSTEMS

by

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B.S. University of Central Florida, 2006

A dissertation submitted in partial fulfillment of the requirements
for the degree in Doctor of Philosophy
in the Department of Chemistry
in the College of Sciences
at the University of Central Florida
Orlando, Florida

Fall Term
2010

Major Professor: Cherie L. Geiger

ABSTRACT

Polychlorinated Biphenyls (PCBs) are a group of 209 congeners that are regulated under the Toxic Substance Control Act. They enter the environment as a result of industrial processes and can travel long distances. PCBs are environmentally persistent and bioaccumulate in animal populations. Painted surfaces are a common point source for PCBs and there are few options for remediating structures painted with PCB-contaminated paint. Removal of the paint can often spread contamination and disposing or burning of large structures is expensive.

Experiments employing reductive dehalogenation through the use of a bimetal have shown that PCBs can be degraded in mild laboratory conditions. This dissertation describes the process of developing an application media that will enable the degradation process reported in literature to be used in a field application. An environmentally friendly reaction environment had to be established as well as the treatment's operating parameters. In collaboration with researchers at the National Aeronautics Space Administration (NASA), Kenney Space Center (KSC), researchers at the University of Central Florida (UCF) developed a bimetallic treatment system (BTS) that can remove and degrade PCBs from painted surfaces.

The technology was evaluated during a field demonstration at a decommissioned Department of Defense facility in Badger, Wisconsin. Samples of treatment paste, paint and concrete were analyzed over a three week period. The PCB concentrations in both the paint and concrete dropped dramatically as a result of the demonstration, and in many instances, were lowered below the EPA action limit of 50ppm.

In the laboratory, additional studies were conducted to further the degradation in the treatment system. Through this process, a novel degradation system was established containing zero-valent magnesium and ethanol acidified with acetic acid. The use of acidified ethanol permitted the degradation to occur with

just magnesium powder and eliminated the use of a bimetal and therefore palladium. The technology was incorporated into a modified treatment system termed Activate Metal Treatment System (AMTS). The AMTS was used on samples from a second field site where paint chips from an manufacturing warehouse in New York state were degraded to thousands of mg/kg (ppm) below their starting concentrations.

To my parents, Kris and Les.

Your never ending love and guidance has made me who I am

To my sister, Leslie.

You continue to inspire me everyday

To my husband, Nick.

You have been with me each step of the way and have made my every dream your own.

Thank you for your patience

ACKNOWLEDGMENTS

I would like to acknowledge various colleagues and collaborators for their input to this dissertation. I thank my collaborators at Geosyntec and NASA, KSC for their contribution to the field study at the Badger Army Ammunition Plant. Both agencies played a pivotal role in the planning and implementation of the project. I would particularly like to acknowledge Geosyntec for images of the remediation sites included in Chapter 4. I would also like to acknowledge the United States Navy for their involvement.

I am very appreciative to my committee members Dr. Andres Campiglia, Dr. Michael Hampton, and Dr. Aldrin Sweeney, all of whom have known me since my undergraduate studies and have continued to guide and encourage me through my graduate work. I would like to acknowledge my colleagues in the UCF Environmental and Industrial lab for their unending support and camaraderie. A special "thank you" also goes out to my husband Nick Saitta who diligently proof read this dissertation through its many drafts.

I am very grateful to have conducted much of my research in collaboration with Michael Gittings who worked endlessly on many of the studies described in this dissertation. I would like to thank him for his expertise and dedication, including long hours in the lab. I could not have done it without his contribution and true friendship. I would like to thank my co-advisor, Dr. Christian Clausen, for his never ending faith in me as well as in my research. He not only is one of the most innovative scientists I have met, but he also has the biggest heart. Most importantly I would like to thank my advisor, mentor, and friend, Dr Cherie Geiger, who has always envisioned what I could become. Her knowledge of chemistry research and leadership is rivaled only by the compassion she has for her students. For that, I will be forever grateful.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF MEDIA/ABBREVIATIONS/NOMENCLATURE/ACRONYMS

AMTS	Activated metal treatment system
ASTM	American Society for Testing and Materials
BAAP	Badger Army Ammunitions Plant
BDL	Below detection limit
BTS	Bimetallic treatment system
C	Carbon
^{o}C	Degree Celsius
cm	Centimeter
DOD	Department of defense
DNAPL	Dense nonaqueous phase liquid
ECD	Electron capture detector
EPA	Environmental protection agency
EZVI	Emulsified zero valent iron
Fe	Iron
FID	Flame ionization detector
ft	Foot
g	Gram
GC	Gas chromatography
kg	Kilogram
KSC	Kennedy Space Center
LC34	Launch Complex 34
LUT	Launch umbilical tower
Mg	Magnesium

min	Minute
ml	Milliliter
MS	Mass spectrometer
MSFC	Marshall Space and Flight Center
NASA	National Aeronautics Space Administration
ng	Nanogram
nm	Nanometer
NM	Non metal
NMTS	Non metal treatment system
PCB	Polychlorinated Biphenyls
PCP	Pentachlorophenol
Pd	Palladium
PEG	Polyethylene glycol
ppm	Parts per million
PRB	Permeable reactive barriers
PTFE	Polytetrafluoroethylene
Sil	Silicon sealant
TATP	Triacetone triperoxide
TCE	Trichloroethylene
TSCA	Toxic Substance Control Act
UCF	University of Central Florida
VOC	Volatile organic compounds
Vp	Vinyl polymer sealant
ZVI	Zero valent iron
ZVM	Zero valent metal

µl	Microliter
µm	Micrometer
PEG	Polyethylene glycol

CHAPTER ONE: INTRODUCTION

Polychlorinated biphenyls

Physical properties

Polychlorinated biphenyls (PCBs) are a group of organic compounds that have the general formula $C_{12}H_{10-x}Cl_x$ where x = 1-10 [1]. There are 209 different ways to chlorinate the biphenyl rings and each individual structure is termed a congener. Congeners with the same number of chlorine atoms are in the same homolog. In each homolog, the positions of the chlorines around the biphenyl rings differ for each congener resulting in various isomers [2]. Figure 1 shows the general structure for polychlorinated biphenyls and indicates the ortho, meta, and para positions [3]. The number of chlorine atoms on the biphenyl backbone determines its properties. For example, highly chlorinated congeners with more than 6 chlorines tend to be thick, greasy waxes that are darker in color. Moderately chlorinated congeners with 5 to 6 chlorines tend to be yellowish, heavy and viscous, while lightly chlorinated congeners with 1 to 4 chlorines tend to be colorless oily liquids [2].

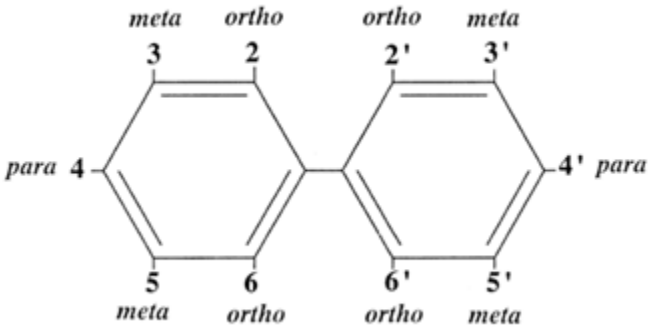


Figure 1: General structure for polychlorinated biphenyl

All polychlorinated biphenyls are synthetic as there are no naturally occurring PCBs [4]. The aromatic structure of PCBs leads them to be extremely stable with low flash points [2]. Additional properties of PCBs include resistance to chemical or thermal degradation and electrical resistivity which made them appealing for industrial processes [1].

Use in industry

PCBs were often produced commercially as complex mixtures containing 60-90 different congeners [5]. The predominate PCB mixtures in the United States were produced under the trade name, Aroclor® from 1930 to 1977 [5]. The Aroclor mixtures were named in a four digit system. The first two digits are the number 12 which represent the 12 carbon atoms that make the biphenyl structure [2, 5]. The last two digits represent the percent weight of chlorine in the compound. For example, Aroclor 1254 is 54% chlorine by weight while 1260 is 60% chlorine by weight. Due to the PCBs' chemical and physical stability, as well as their dielectric properties, Aroclors have been used in a variety of applications including transformers, capacitors, caulking, paints, and pesticides [6, 7]. It is estimated that 1.2 to 1.3 million tons of PCBs were produced worldwide with 640,000 tons produced in the United States [8]. Various studies have approximated that 15% of the PCBs produced in the United States are thought to have entered the environment as a result of disposal, both legal and illegal, as well as through accidental release [1, 2].

PCBs in the environment

PCBs can enter the environment under various circumstances. Environmental exposure could have occurred during manufacture, use, transport, or disposal of PCB containing materials during their industrial use. Accidents, including leaks and fires, may also introduce PCBs into the environment. Waste incineration is attributed to the emission of PCBs in the air, in addition to emissions from treatment storage, disposal facilities, and reclaimed metal facilities [2, 6] Once in the environment, PCBs can travel long distances and have been found in air, water, soil, and food [9]. Due to their organic nature, PCBs are not very soluble in water with the solubility in the parts per million, ppm. Solubility tends to decrease

with an increasing number of chlorines and it ranges between 0.007ppm to 6ppm. As a result, PCBs partition into the organic matter in soils and sediments which act as PCB reservoirs [5]. Overtime, the sorbed PCBs may become more available and therefore act as a long-term threat to the environment [10]. In addition to PCBs being hydrophobic, they are also lipophilic, which makes them particularly prone to bioaccumulation [2]. In fact, fish can have hundreds of thousands times higher PCB levels than their surrounding environment [2]. Contaminated fish have been the source for PCB exposure to both animals and humans. This can have a wide range of effects on animal health and populations. For example, high concentrations in sea birds have been reported to inhibit calcium production and therefore can cause eggshell thinning [2].

Health effects

Animals and humans absorb PBCs through the skin, lungs and gastrointestinal tract [2]. Though the commercial mixtures of PCBs have been at the forefront of these studies, the most toxic congeners have been identified as having between 5 and 10 chlorines [2]. There is additional evidence that the few PCB compounds that display a planer, or dioxin-like, conformation may have a similar toxicity, though this is more apparent in studies involving animals [1]. The precise effect that PCBs can have concerning human health is difficult to determine. Research involving workers exposed to high levels of PCBs as well as people who have consumed a large amount of fish with a high concentration of PCBs often contains numerous variables. PCB exposure at work may occur alongside exposure to other harmful chemicals and is therefore difficult to determine which side effects are the results of PCBs alone. There have been studies that have correlated human PCB exposure with liver problems, skin lesions (including chloroacne), changes in the immune system as well as causing irregular ocular effects. Laboratory studies involving animals have indicated that PCBs may also have an effect the endocrine, central nervous, and reproductive systems [9, 11]. PCBs are classified as a probable human carcinogen according the Environmental Protection Agency (EPA). They have been associated with cancer of the liver, intestines, and skin in humans through case-controlled studies of occupational exposure in retrospect cohort

mortality studies. In addition, there is conclusive evidence of the carcinogenic effect that PCB mixtures have on animals including cancer of the liver and thyroid

Addressing PCB contamination

Due to the environmental persistence and lack of natural degradation, the production and use of PCBs has been banned in many countries. Both the manufacture and importation of PCBs were discontinued in Sweden in 1970 and in Japan in 1972 [2]. In 1976, the Toxic Substance Control Act (TSCA) prompted various federal laws that addressed the regulation of PCBs in the United States [12]. Although the production of PCBs has ceased, PCB contaminated materials are still present in the environment [11]. Painted surfaces can be a major point source for PCB environmental contamination [13, 14]. Paint flakes, as a result of renovations, weather conditions, and sand blasting, can lead to high concentrations in storm water and soil [4, 13]. Cleaning PCBs in soil and sediments through dredging, capping and bioremediation is complex, difficult and expensive [2, 3, 5, 10]. Therefore, it is ideal to remove and remediate the PCBs from the painted surface before they get into the environment.

Current remediation techniques and their issues

Structures painted with PCB-contaminated paint pose a problem to those who are legally responsible, including government agencies like the Department of Defense (DoD). This is because the Toxic Substance Control Act requires that PCB-contaminated materials be greatly degraded or discarded in one of the few licensed landfills [12]. To date, there are very few remediation options for contaminated building materials. Disposal methods and alternative remediation techniques involve their own unique limitations.

Landfills

There are a few types of landfill options available depending on the building structure and PCB concentration. State permits can be obtained, with risk-based approval, to dispose of PCB contaminated materials in a site-owned and operated landfill. The threat of PCBs leaching into the environment,

however, does not go away and the long term environmental liability remains with the landfill. Hazardous waste landfills are the most common type of landfill for PCB contaminated materials although the environmental liability still exists. These types of landfills charge by the amount of material disposed and are therefore cost-prohibitive for large structures. Only if the PCB concentration is below 50ppm may the materials be disposed of in a state-approved landfill.

Removal of Paint

The removal the paint by sandblasting or water blasting simply transfers the PCBs into a different medium. Sandblasting also produces PCB contaminated dust that can spread to other surfaces and the environment [7]. Not only does this increase the potential for PCBs to further contaminate the environment through air or surrounding media, but there is production of PCB contaminated sand or water. In addition, PCBs are often transferred into the superficial portions of the painted structure. Therefore, removing the paint does not ensure the removal of all of the PCBs in the structure.

Smelters and Recovery Ovens

Incineration of painted material can be costly for large structures. In order for a structure to be disposed of in a smelter or recovery oven, permission would be required to cut the structure into small pieces and transported. This could allow for further environmental contamination and high costs associated with labor. Additionally, incomplete incineration of PCB contaminated materials can emit other toxic compounds like dibenzodioxins and dibenzofurans [15].

Emerging technology

Due to the issues resulting from the methods described above, in-situ remediation of contaminated painted structures is rare. Researchers at the University of Central Florida (UCF), in collaboration with the National Aeronautics and Space Administration (NASA) Kennedy Space Center (KSC), have recently developed an in-situ method that can be customized for the removal of PCBs from painted structures and equipment. The remediation technology consists of a treatment paste that can be applied directly to the

structure and removed after the remediation period. The treatment system is based on reductive dehalogenation by zero valent metals.

Reductive metal systems

Zero-valent metals

Research has been conducted for decades concerning the degradation of halogenated hydrocarbons through zero-valent metals (ZVM). Many of these studies involve reductive dehalogenation of chlorinated aliphatics [16-19]. In this process, the redox couple between the zero-valent metal and the dissolved ion drives the reaction.

$$M(0) \rightarrow M^{n+} + ne^-$$

$$R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^-$$

Equation 1: Redox reaction involving a zero-valent metal

Equation 1 shows the dissolution of the metal in solution followed by the hydrogenation of the alpha carbon [20]. The result of this process includes dechlorinated, or lower chlorinated products. In environmental remediation, iron and magnesium are common metals chosen for this type of reaction due to their low cost and mild environmental impact.

Zero-valent iron (ZVI) specifically, has been the focus of a large body of research revolving around the remediation of chlorinated organics, nitrates, perchlorates and heavy metals [16, 21-24]. Permeable reactive barriers (PRB) composed of ZVI were one of the first successful field technologies that focused on degrading groundwater contamination through the use of zero-valent metals.

Degradation through ZVI is not without its limitations. The oxidation of Fe^0 to Fe^{2+} is essentially metal corrosion which, in turn, alters the surface of the metal. The corrosion acts as the anodic half-reaction which interacts with the cathodic half-reaction according to the available oxidizing agents. In pure water,

under anaerobic conditions, oxidizing agents include H^+ and H_2O while in aerobic conditions, reduction occurs through O_2 [10]. Because of this, anything that affects the corrosion of the metal will also affect the metal's ability to dehalogenate hydrocarbons. With this said, washing the metal surface with dilute acid has been shown to increase the rate of dehalogenation probably due to the removal of the unreactive oxide layer formed on the metal surface. [25, 26]

The use of zero-valent magnesium has been reported to degrade halogenated organics without some of the limitations of ZVI. Equation 2 shows the more negative standard reduction potential of magnesium compared to iron which leads it to be thermodynamically favored as a reducing agent.

$$Fe^{2+} + 2e^- \rightarrow Fe^0 \qquad E^0_{red} = -0.44V$$

$$Mg^{2+} + 2e^- \rightarrow Mg^0 \qquad E^0_{red} = -2.37V$$

Equation 2: Standard reduction potentials of magnesium compared to iron

In addition to the largely negative reduction potential, magnesium also experiences limited surface oxidation compared to iron which makes it a good choice for this type of remediation [27]

Degradation of aromatic compounds through the use of ZVM has been proven to be more difficult than degrading halogenated alkanes and alkenes [16]. PCBs have been reported to degrade by ZVI, however, this was done within extreme parameters including high temperatures and in the absence of oxygen or water [28]. The extreme parameters would make it unappealing for field use Efforts to enhance the degradation process for use at ambient temperature and pressure inspired the incorporation of two metals which form a reductive catalytic surface called a bimetal. It was found that the rate at which dechlorination occurred by ZVI was enhanced by the addition of the catalyst, palladium [29-31]

Bimetals

Bimetallic systems consist of a zero-valent metal with a negative reduction potential which corrodes in the presence of water to produce molecular hydrogen. It also contains a metal with a high reduction

potential that acts as a reducing catalyst. The hydrogen that is formed by the zero-valent metal is absorbed onto the solid catalyst and forms a metal hydride and, in the process, dehalogenates the target compound [32]. Common bimetals consist of zero-valent metals including magnesium, iron or zinc paired with common hydrogenation catalysts like palladium or nickel, although other combinations have been reported in literature [33-36]

The benefit of using a bimetal is its ability to degrade chlorinated organic compounds at room temperature and pressure while in an oxygenated environment [32]. For example, Aroclor 1260 and 1254 were reported to completely degrade at ambient temperatures by Fe/Pd in a methanol/water/acetone system within 10 minutes producing biphenyl and chloride ions [34]. Zhang also used Fe/Pd, but this time on the nanoscale, to degrade Aroclor 1254 at ambient temperatures [37, 38].

Bimetals are commonly prepared through electrodeposition of the catalyst onto the metal surface. In this process, the zero valent metal is placed into a solution containing the catalytic material and due to the chemical potentials, reductive precipitation occurs and the catalyst is plated onto the metal. One study reported the preparation of Fe/Pd by stirring hexachloropalladate, K_2PdCl_6, with iron powder for a few minutes until the iron was approximately 0.05% Pd by weight [34]. Patel et al prepared Mg/Pd in a similar way and used it to degrade pentachlorophenol, PCP, to phenol [32]. Etching the metal surface before exposure to the catalytic material has also been reported [26, 39].

An alternate method of producing bimetal particles involves mechanically alloying the materials through high-energy ball milling. During this process, a container that holds at mixture of powders (at least one being a metal) and stainless steel ball bearings is vigorously shaken and the particles are repeatedly flattened, cold welded, fractured and rewelded [40]. The milling process in of itself is a complex one that is dependent on specific parameters including the type of milling, type of material to be milled, number of particles and ball bearings in the canister, milling speed and time, and dimensions of the milling components. When two steel balls collide trapping some amount of material between them, enough

energy may be provided to break the particles into smaller fragments or initiate a welding effect [40]. Mechanical alloying, therefore, entails a material transfer to achieve a homogeneous alloy [40]. During the milling process, the material may experience various transformations and types of welding before reaching an equilibrium [40, 41].

Mechanically alloyed Mg/Pd has been used in studies including the degradation triacetone triperoxide (TATP) in a water/methanol solution [42]. Similar Mg/Pd particles were also used to degrade monochlorinated biphenyls and a hexachlorobiphenyl in methanol [43, 44]. These studies were done to further understand chemical degradation in order to one day apply it to environmental remediation.

Remediation technologies including the bimetallic treatment system (BTS)

Once the chemical degradation has been established in the laboratory, it is often incorporated into an application technology which determines how it will be used in the field. This step usually involves a scale-up of laboratory studies and is founded on the specific parameters defined by the type of site being remediated. For example, remediating viscous liquids, like contaminated sludge, through the use of a solid catalyzed reaction is difficult due to the lack of contact between the catalyst and the target compound. However, Graham and Jovanovic incorporated what they knew about zero valent bimetallic catalysts with a reactor system to create a novel way for treating soil and sediment. Their research explored the use of the bimetal Fe/Pd entrapped in alginate beads which was placed in a magnetically stabilized fluid bed reactor to degrade p-chlorophenol in aqueous solutions with and without soil [45].

Emulsified Zero-Valent Iron (EZVI) is another example of a technology that applied the understanding of reductive dehalogenation with the parameters of a specific remediation environment. Aquifer material contaminated with chlorinated dense non aqueous phase liquid (DNAPL) is often difficult to treat with ZVI due to the limited interactions between the iron particles and the hydrophobic DNAPL. In a recent field demonstration, GeoSyntec, UCF, and NASA, KSC demonstrated that when ZVI particles in water

are surrounded by an surfactant/oil-liquid membrane, it is protected from surrounding ground water long enough to allow the TCE to diffuse to the interior of the droplet and degrade [21].

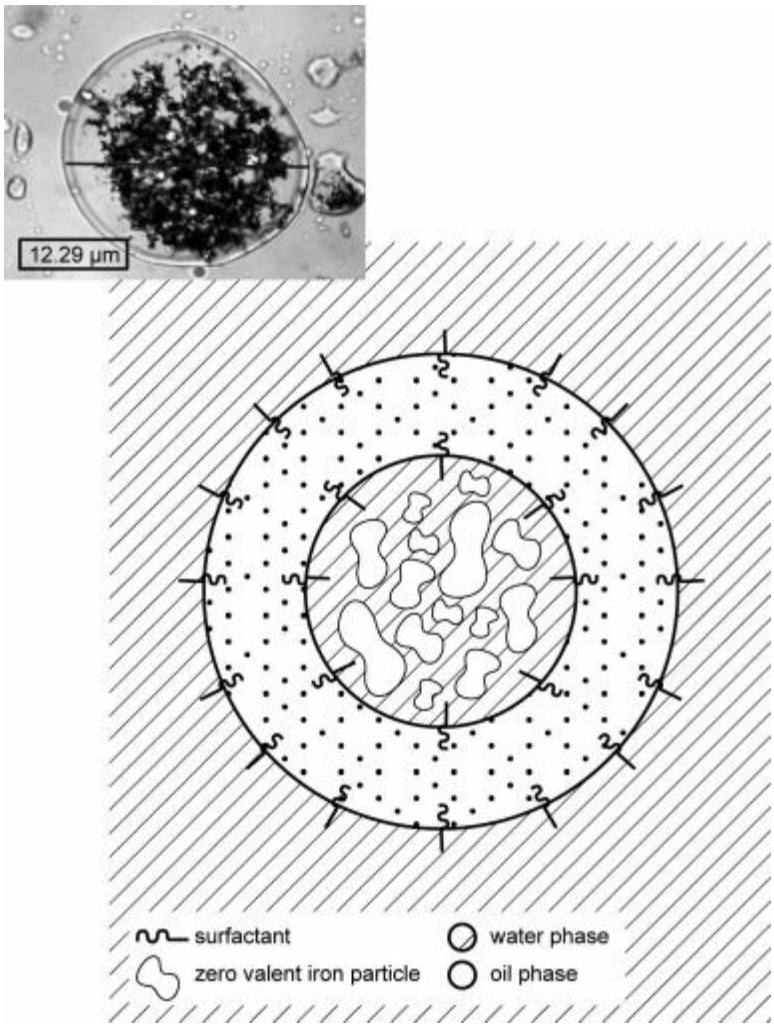


Figure 2: Image of EZVI along with a representation of the components of the droplet (reprinted with permission)

Figure 2 displays a microscopic picture of an EZVI droplet as well as a schematic that demonstrates the components of the micelle [21]. The EZVI was able to reduce ground water concentrations from 57-100% at depths of up to 26 feet within 5 months.

Previous studies

The National Aeronautics and Space Administration (NASA) Kennedy Space Center (KSC) investigated the use of solvent-based PCB removal systems for painted structures at their operating centers. Launch Umbilical Towers (LUT) at KSC and main engine test stands at Marshall Space Flight Center (MSFC) were part of the preliminary studies funded by NASA's Environmental Program Office and Office of Space Flight. Both of these studies investigated the use of a bimetallic treatment system (BTS) in the removal and degradation of PCBs on painted metal parts utilized during the Apollo Program.

The treatment of PCB-contaminated paint at NASA's Launch Umbilical Tower involved the bimetal, Mg/Pd, incorporated into a water-in-solvent emulsion. This emersion technique was developed for structures that were intended to be broken down but a technology was needed for structures that would remain intact. Therefore, the formulation was modified from a bimetal emulsion to a bimetallic treatment system paste that could be applied and removed after the treatment period.

Bimetal treatment system (BTS) paste

The homogeneous nature of the bimetal treatment system (BTS) paste is based on the chemical degradation process which utilizes the bimetal Mg/Pd in the presence of ethanol. Figure 3 is an illustration of the two intended functions the BTS serves including the removal of PCBs from contaminated paint and the degradation of PCBs into inert byproducts.

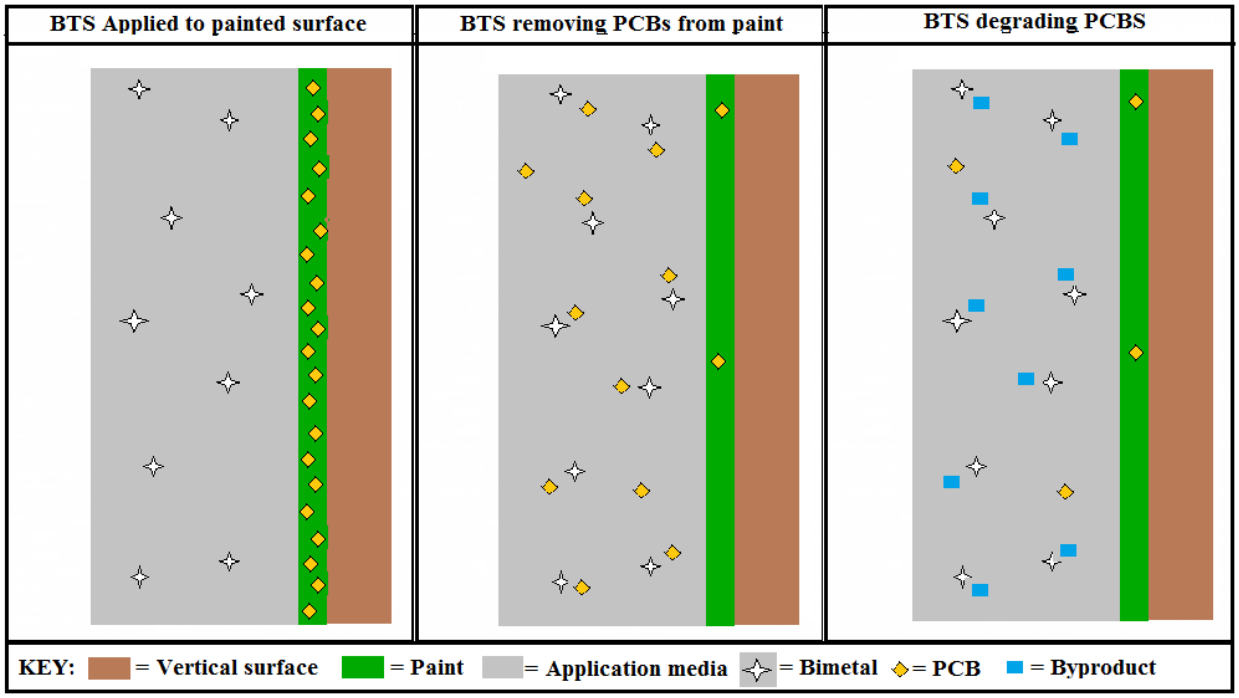


Figure 3: Illustration of the intended use of BTS paste

The BTS consists of the bimetal and solvent system suspended in a viscous application media which allows it to remain uniform throughout. Bulking agents include calcium stearate and polyethylene glycol 8000. The solvent system includes limonene, a natural paint softener, which softens the paint while the BTS is in contact with the contaminated surface and allows the PCBs to partition into the treatment system. The majority of the solvent consists of absolute ethanol, which can solvate large amounts of PCBs and is environmentally friendly. Once the PCBs are in the treatment system, the ethanol is to act as a proton source for degradation with the bimetal through hydrodehalogenation. The concept of the BTS is the inspiration for the laboratory and field studies portrayed in this dissertation.

Dissertation Objectives

In order to determine the scope of this research, a list of objectives has been developed to guide the experiments described in this dissertation. The studies expressed in this paper are intended to:

- Expand on existing application media to optimize remediation on vertical concrete and metal surfaces
- Develop ways to make custom treatment system formulations for different types of contaminated sites
- Define parameters in which the technology can be used
- Report on site specific successes and difficulties regarding the scale-up process
- Analyze the effectiveness of the treatment system on actual contaminated samples for field use
- Continue laboratory studies to further enhance PCB degradation

In the process of conducting the research, however, additional objectives were added to:

- Report the extent to which PCBs degrade in a newly developed acidified ethanol system containing magnesium powder
- Develop an Activated Metal Treatment System (AMTS) and analyze the degradation that can occur compared to a Bimetallic Treatment System (BTS)
- Test the AMTS on samples from a 2nd field demonstration
- Suggest future paths of study to take the technology further

CHAPTER TWO: MATERIALS AND EXPERIMENTAL SETUP

Bimetal production

In order for the Mg/Pd bimetal to be a realistic component of a field demonstration, a cost effective and efficient method was used to prepare the bimetal. The Mg/Pd bimetal that was utilized in the studies presented in this dissertation was produced by mechanically alloying the materials in a scaled-up ball mill process. Ball milling procedures were based on the optimization of this process which was previously developed in-house [41, 46]. Metals were loaded into galvanized steel pipes that were 17.80cm in length and 5.03cm in internal diameter. Stainless steel ball bearings ($1.6cm^3$) were placed in the pipe and the ends were fitted with steel caps. The scaled-up mill comprised of a Red Devil 5400 twin arm paint shaker with cork end plates designed to hold the canisters in place. Figure 4 displays the components of the milling process including the steel canisters and cork end plates [41].

(a) **(b)**

Figure 4: a) steel canister b) steel canisters between cork end plates hooked up to the paint shaker ready for the milling process

To make the Mg/Pd bimetal, the canisters were cleaned with ethanol and dried with acetone. Magnesium, with a mass of 76.5g, was placed in each canister containing 16 ball bearings along with 8.5g of 1% palladium on carbon graphite. The canisters were flushed with nitrogen before being capped and placed on the paint shaker. The milling time was 30 minutes and the final alloy consisted of 91.8% Mg, 0.08% Pd, and 8.12% C. After each batch, the canisters were cleaned by shaking the ball bearings in ethanol for 15 minutes on the paint shaker.

Treatment system preparation

The different types of treatment systems were made in a range of batch sizes through scaling up or down while maintaining the percentages of each component in the mixture. The procedure includes combining the bulking agents in one beaker, and the solvent system in the other, before combining both of them together. The metal used to activate the treatment system was always coated with glycerol before being introduced to the treatment system to slow the initial reaction as a safety concern for the handler. The following procedures are intended to produce a small batch suitable for vial studies.

Non-metal treatment system

The basic procedure to make the non-metal treatment system began with coating 10.0g of sodium polyacrylate with 5.0g of glycerol in a large beaker. The mixture was stirred until the solid was completely coated. In a separate container, 10.0g of calcium stearate was combined with 5.0g of polyethylene glycol 8000. In a third container, 68.16ml of absolute ethanol was combined with 7.58ml of limonene and 0.765ml of glacial acetic acid. Once all of the components were measured into the three containers, the container with the solid calcium stearate and polyethylene glycol was poured into the container with the solvent. While stirring, this mixture was poured into the first container holding the sodium polyacrylate and glycerol. The combined mixture was stirred to ensure that none of the glycerol remained stuck to the bottom. At this point, the system was a very fluid white liquid. The contents were poured into an air tight container and sealed. The treatment paste would thicken within a half hour and would remain at the appropriate consistency for at least a year if kept sealed.

Activation with metal and acidified ethanol

To make metal-activated paste, including paste with Mg/Pd, Mg/C, and Mg, equal amounts of metal and glycerol were combined. Once the metal was completely coated with glycerol, 1.2 g of the metal/glycerol mixture was combined for every 10g of NMTS. For example, 20g of NMTS would be combined with 2.4g of a Mg/glycerol mixture. Next, acidified ethanol that was 10% glacial acetic acid (v/v) was added to the mixture in a 10% volume to mass ratio with the metal treatment system. For example, if 20g of NMTS was combined with 2.4g of metal and glycerol, it would have a total mass of 22.4g. Therefore, 2.24ml of 10% acidified ethanol would be added to the mixture to finish the activation process.

Five gallon batches for field test

To make the five gallon batch of BTS used in the field study, 1.6kg of sodium polyacrylate was combined with 0.8kg of Mg/Pd powder coated with 1.6kg of glycerol. This mixture was stirred until uniform. In a separate bucket, 1.6kg of calcium stearate was combined with 0.8kg of polyethylene glycol 8000. In a third container, 9.914L of absolute ethanol was combined with 1.224L of limonene and 110ml of glacial acetic acid. The container with the solvent was poured into the bucket containing the solid calcium stearate and polyethylene glycol 8000. Once combined, the mixture was immediately poured into the original bucket containing the glycerol coated Mg/Pd and sodium polyacrylate. The entire mixture was stirred with a drill affixed with a stir attachment. Within approximately 5 to 10 minutes, the reaction between the acidified ethanol and the Mg/Pd began to produce hydrogen gas. The treatment paste was occasionally stirred to release the gas. After an hour, the container was sealed.

The five gallon NMTS produced for the field study was produced in a similar manner except without the bimetal and with half of the glycerol. Therefore, the first container contained 1.6kg of sodium polyacrylate and only 0.8kg of glycerol. The second and third containers were made as described in the previous paragraph. All of the components were combined in the manner described above as well.

Chemicals

Neat PCB standards were purchased from Accustandard (New Haven, CT). Absolute ethanol, glacial acetic acid, ACS grade sulfuric acid, Optima© grade toluene, calcium stearate powder, polyethylene glycol (PEG) 8000, glycerol, and (+)-limonene, stabalized (Tech.), 95% were acquired from Fisher Scientific (Pittsburgh, PA). Magnesium metal (2-4 µm diameter) was purchased by Hart Metals, Inc (Tamaqua, PA). Palladium on carbon (graphite) 1% was received from Engelhard (Iselin, New Jersey) Poly(acrylic acid sodium salt) was purchased from Aqua Solutions (Deer Park, TX). Olympic® Fast Hide® with ultra semi gloss white paint and Dupli-Color® Truck Bed Coating were bought commercially.

PCB extraction and analysis methods

Extraction for neat metal studies

A portion of the studies involved PCBs being extracted from 5.00ml of acidified ethanol combined with 0.25g of metal, the type of metal varied by experiment. These studies were extracted using 5.00ml of toluene which was added to the PCB solution and shaken by hand. After being shaken for 2 minutes, 4.00ml of the solution was pulled through a glass syringe with an affixed Millex® 0.45µm nylon syringe filter. The filtered solution was placed in a centrifuge tube at which time, 2.00ml of de-ionized water was added. The solution in the centrifuge tube was briefly shaken to mix and then centrifuged for 5 minutes; at which time the top organic layer was removed and diluted for PCB analysis.

Extraction for solid samples and treatment system paste

The majority of experiments involved PCBs being extracted from solid paint chips, concrete, or treatment system paste. These samples were extracted in 10.0ml of toluene using EPA Method 3550 (Ultrasonic Extraction) [47]. After being sonicated for 90 minutes, samples were centrifuged for 5 minutes and decanted. The supernatants were subjected to a one-to-one (v/v) sulfuric acid clean up followed by a one-to-one (v/v) potassium permanganate clean-up as outlined in EPA Method 3665 (Sulfuric Acid/Permanganate Clean-up) [48] .

PCB analysis through Gas Chromatography/Electron Capture Detector

Most of the samples were analyzed using a Perkin Elmer AutoSystem XL GC/FID/ECD equipped with an autosampler. The GC was outfitted with a 30m Restek Rtx-5 column (Crossbond 5% diphenyl - 95% dimethylpolysiloxane, 0.25 mmID, 0.25um df). Samples were run in duplicate unless stated otherwise. GC/ECD parameters included an injector and detector temperature of 275^{o}C and 325^{o}C respectively. The initial temperature of the GC oven was held at 120^{o} C for 1 min. The temperature was ramped at 20^{o}C min^{-1} until 200^{o}C, 10^{o}C min^{-1} until 270^{o}C, and at 20^{o}C min^{-1} until reaching a final temperature of 300^{o}C. The makeup gas consisted of ultra high purity nitrogen at a flow rate of 30ml min^{-1}. The flow rate of the carrier gas, helium, was 1.3 ml min^{-1}

PCB analysis through Gas Chromatography/Mass Spectrometry

Byproduct analysis was done with a Thermo Fisher Scientific GC/MS equipped with an autosampler and outfitted with a 30m Restek Rtx-5 column (Crossbond 5% diphenyl - 95% dimethylpolysiloxane, 0.25 mmID, 0.25um df). The method to detect PCBs started with an initial oven temperature at 100^{o}C which was held for 2 min. There were two temperature ramps, the first one raising 15^{o}C min^{-1} until 160 degrees and the second one at 5 ^{o}C min^{-1} until a final temperature of 270^{o}C. The method to detect biphenyl began with an oven temperature of 115^{o}C which was held for seven minutes. There were two temperature ramps, the first one rising 40^{o}C min^{-1} until 200^{o}C and the second one at 10^{o}C min^{-1} until reaching a final temperature of 270^{o}C. The carrier gas, helium, was 1.2 ml min^{-1}.

PCB Quantification

PCB concentrations were quantified as described in EPA method 8082A (Polychlorinated Biphenyls (PCBs) by Gas Chromatography)[49]. Single congener concentrations were determined by one peak area while Aroclor concentrations were determined by summing the peak areas of the five most prominent peaks [49].

CHAPTER THREE: LABORATORY STUDIES TOWARDS FIELD APPLICATION

The first half of the research project, as described in the dissertation objectives, lead to the scaled-up field study of the BTS technology. The site of the field study was planned to occur at a DOD facility in the northern part of the United States in early spring of 2008. Samples of concrete, metal and wood, all painted with PCB-contaminated paint, were shipped to the University of Central Florida (UCF) for initial analysis. Aroclor 1254 and Aroclor 1260 were the two commercial PCB mixtures found in the contaminated paint. The following studies were done in the laboratory to customize the treatment system for the DOD site as well as to define the operating parameters.

PCB degradation through magnesium/palladium bimetal

Experiments involving only the components necessary for PCB degradation established the starting point of the research project. The idea was to degrade PCBs using the simplest system before moving toward the more complex matrix of an application media. If PCB degradation could not occur in solution at ambient temperatures in aerobic conditions, the reaction would have little prospect of developing into an effective in-situ remediation method. Prior to this point, no PCB degradation had been observed in pure ethanol at ambient temperatures and pressures. Acidified solvents had been shown in literature to increase degradation of chlorinated organics, so a small amount of acetic acid was added to the reaction mixture.

Initial neat Mg/Pd study

The initial study involving acidified ethanol began with 0.25g of Mg/Pd bimetal in each 20ml sample vial. Exactly 4.95ml of a PCB spiked ethanol solution with an Aroclor 1254 concentration of 50 ng/µl, was added to the metal and combined with 50µl of glacial acetic acid. Duplicate samples were extracted at the 0hr and 3day time points. Figure 5 displays GC/ECD chromatograms for the 0hr and 3day samples. The peak areas are significantly lower and degradation is apparent.

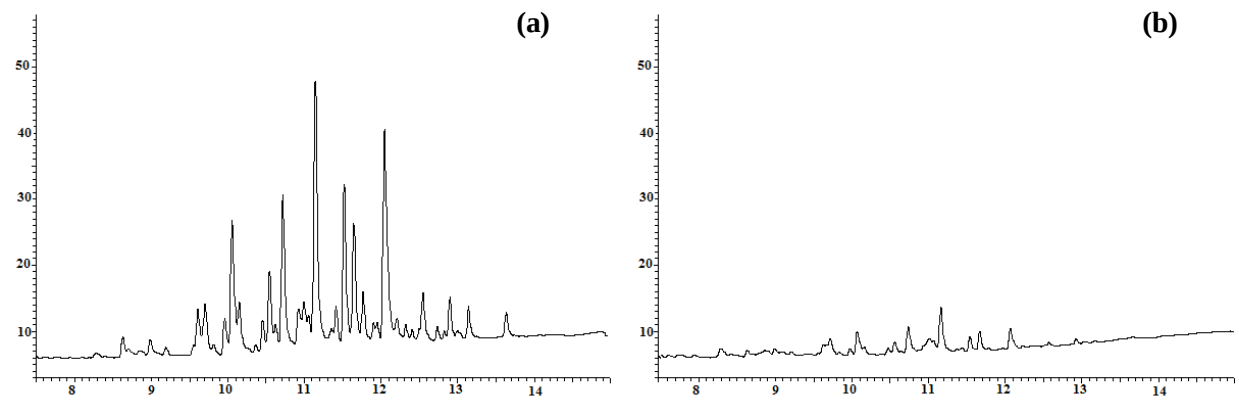


Figure 5: Aroclor 1254 with Mg/Pd in acidified ethanol a) 0hr b) 3day

Aroclor 1254 contains a mixture of PCB congeners which separate during the gas chromatography portion of the analysis process. Each peak displayed on the chromatogram represents at least one type of PCB congener, keeping in mind that PCB congeners have the ability to co-elute. The peak pattern displayed on the chromatogram is unique to the mixture of PCBs and will remain the same at varying concentrations. The lower chlorinated congeners elute first and are detected at the earlier retention times. The more chlorinated congeners usually appear at the later retention times. Previous research has reported that chlorines are removed from the biphenyl rings in a sequential manner [33, 35, 39, 50]. Higher chlorinated PCBs have been reported to dehalogenate before lower chlorinated congeners. Therefore, when observing degradation in PCB mixtures, like Aroclors, the peak areas of higher chlorinated congeners often initially decline while the peak areas of lower chlorinated congeners increase.

In an effort to gain a better understanding of the degradation process, the experiment was repeated with more time points. Figure 6 displays the Aroclor 1254 concentration (C/C^o) over time. More than 99% of the five peaks used for Aroclor quantification were degraded within 48 hours.

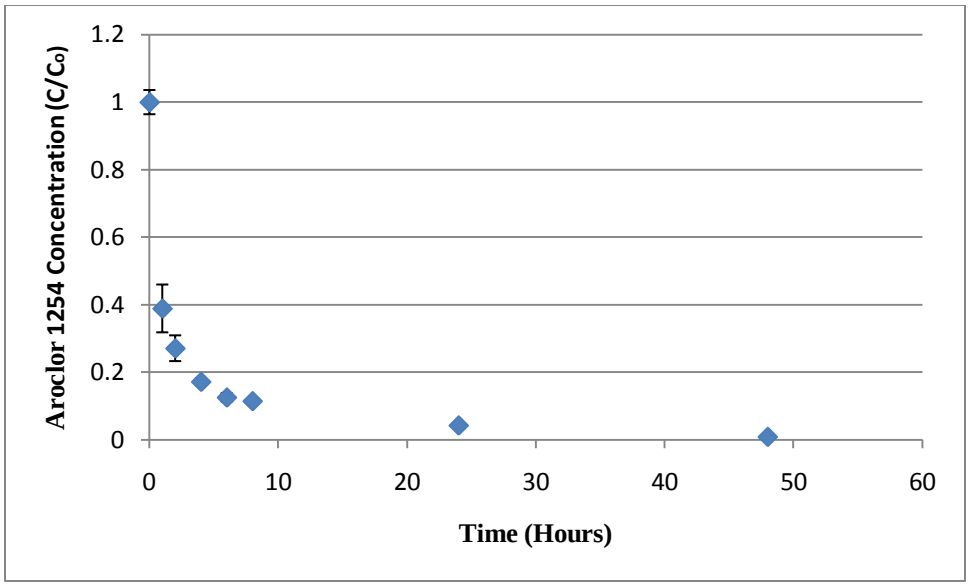


Figure 6: PCB concentration over time while reacting with Mg/Pd

Figure 7 shows the chromatograms from six of the time points. In agreement with previous works, the peaks at later retention times decrease while the ratios of earlier peaks increase. New peaks are also formed in front of the initial PCB envelope.

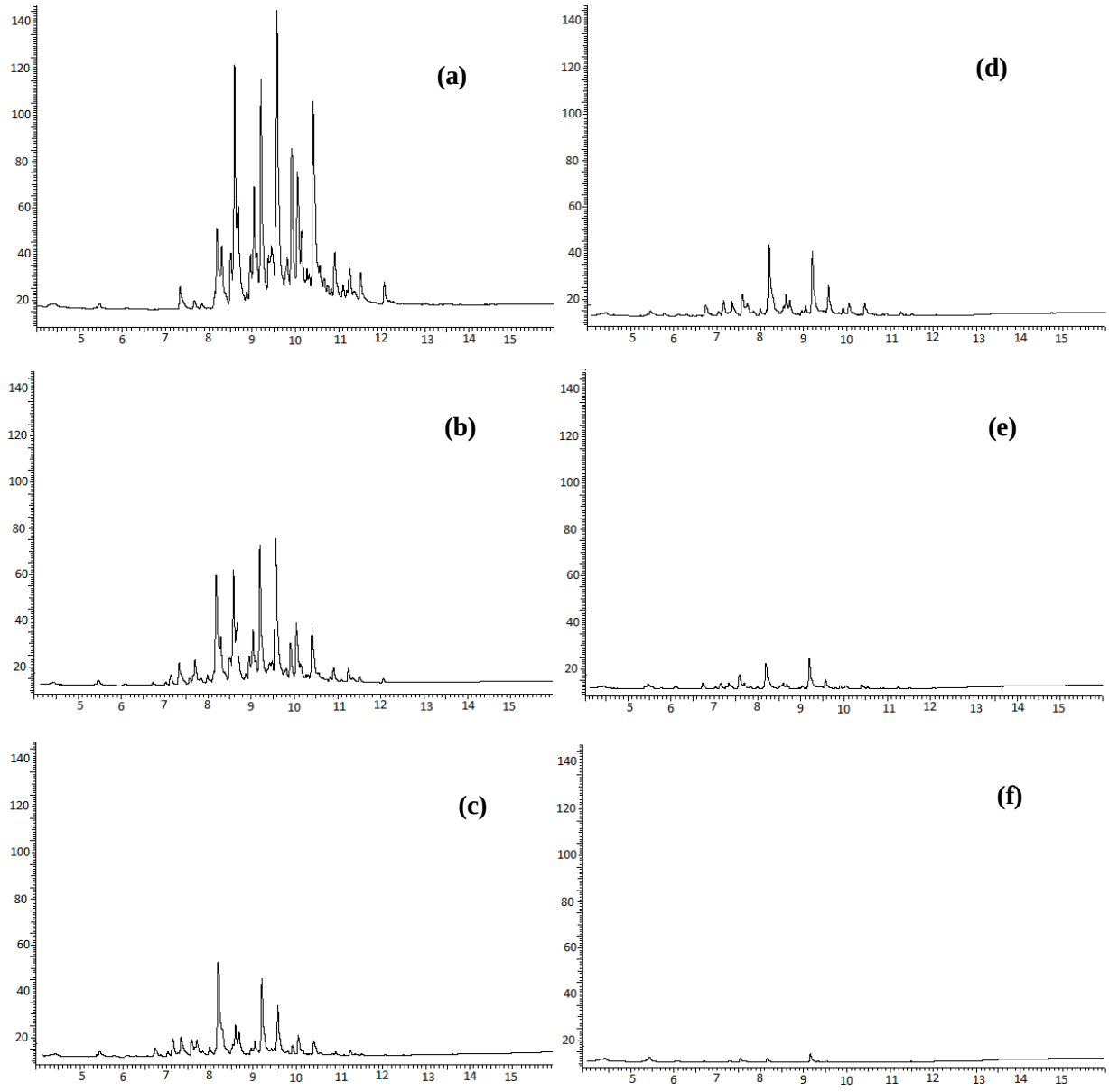


Figure 7: Chromatograms from Aroclor 1254 reacting with Mg/Pd in acidified ethanol

a) 0hr b) 1 hr c) 4 hr d) 8 hr e) 24 hr f) 48 hr

Once it was established that PCBs degrade in acidified ethanol, the reaction matrix was modified toward an effective application media.

Field study preparation

The application media developed for the project was founded on previous studies aimed at remediating PCBs from painted metal. As stated previously, the UCF/NASA team created a BTS emulsion to immerse painted metal parts as a remediation technique. This was modified into a BTS paste that was designed to be applied to a vertical surface during the remediation process and is therefore referred to as the 'apply and seal method'. Notice that the previous studies that utilized BTS involved contaminated paint on a metal surface. The DOD facility in question, however, contained painted metal, concrete and wood. Initial attempts aimed at PCB removal from painted concrete revealed that the treatment system would dry out even when sealed. The reason for this was unknown but it was thought to be a result of the solvent leaching through the pores in the concrete. Therefore, the treatment system needed to be adjusted to treat porous materials. The following studies describe the process of developing a custom treatment system for porous material as well as optimal procedures for field use. In order to simplify the experiments, the matrix itself was developed before being activated with the bimetal component. The inert matrix is referred to as the non-metal treatment system, NMTS.

Toward a solvent-retaining treatment system

The removal capability of the BTS and NMTS ceases in the absence of solvent. Due to the porous nature of the concrete, numerous materials, including cellulose pulp and wood chips, were tested as additives to the treatments system in attempts to retain solvent. The most effective was the incorporation of sodium polyacrylate, the superabsorbent polymer commonly used in baby diapers. Three variations of non-metal treatment paste were prepared in an effort to obtain qualitative data about the best formulation with regard to solvent retention. The NMTS without any additives was compared to NMTS with sodium polyacrylate as well as to NMTS with sodium polyacrylate and cellulose pulp in the proportions displayed in Table 1.

Table 1: Chemical components and their corresponding percentages by mass for three types of non-metal treatment system

Non-Metal Treatment System (no additives)		**Non-Metal Treatment System (with sodium polyacrylate)**		**Non-Metal Treatment System (with sodium polyacrylate and cellulose pulp)**	
Component	% mass	Component	% mass	Component	% mass
Glycerol	11.64	Glycerol	10.43	Glycerol	10.42
Calcium Stearate	11.64	Calcium Stearate	10.43	Calcium Stearate	10.42
Polyethylene glycol	5.82	Polyethylene glycol	5.22	Polyethylene glycol	5.22
Solvent	70.00	Solvent	63.51	Solvent	63.51
		Sodium polyacrylate	10.43	Sodium polyacrylate	5.22
				Cellulose pulp	5.21

The experimental setup for this study consisted of four sections of each type of paste applied to a slab of unpainted concrete and sealed with five coats of vinyl sealant (as discussed later in this chapter). After three days, the sealant was peeled away from one section of each type of paste. All three types of treatment system retained solvent in this timeframe. Two samples from each type of treatment paste were then observed on the eighth day. The paste with the added sodium polyacrylate retained the most solvent while the treatment system with no additives was drier. The treatment system with added cellulose pulp and sodium polyacrylate was only slightly damp as the cellulose did not appear to be helping in solvent retention. After fifteen days, the remaining samples were unsealed and observed. By this time, the treatment system with cellulose pulp and sodium polyacrylate as well as the treatment system with no additives were dry, hard and brittle. The treatment system with the added sodium polyacrylate, however, was still very moist. These preliminary results prompted additional experiments to determine the physical properties of the modified treatment system. The rest of the treatment pastes discussed in this paper, both with metal and without, contained sodium polyacrylate.

Treatment Sealant

The treatment system must be sealed to minimize solvent loss. Previously, in lab studies and in small field tests, the treatment system was sealed with aluminum foil. This proved to be labor intensive, time consuming, and not suitable for large scale remediation sites. A series of water-based latex paints were tested as sealants due to their ease of application on the surface without containing volatile organic compounds (VOCs). A sufficient seal was not achieved so the use of organic solvent based paints was attempted. Finally, a vinyl polymer formulation that is sold as a commercial truck bed liner was found to be a suitable sealant for the treatment system. Figure 8 shows two sections of NMTS applied to a metal surface. Figure 9 shows the same metal piece treated with NMTS before and after application of the vinyl sealant.

Figure 8: NMTS on painted metal part

(a) **(b)**

Figure 9: NMTS a) before being sealed b) after being sealed with vinyl sealant

In order to determine the optimal thickness of the treatment paste as well as the number of sealant coats an experiment was conducted where 20 samples of NMTS with an area of approximately 4cm^2 were applied to a slab of concrete and sealed. Each sample varied in the thickness of the treatment paste in addition to the number of sealant coats and was monitored over 14 days.

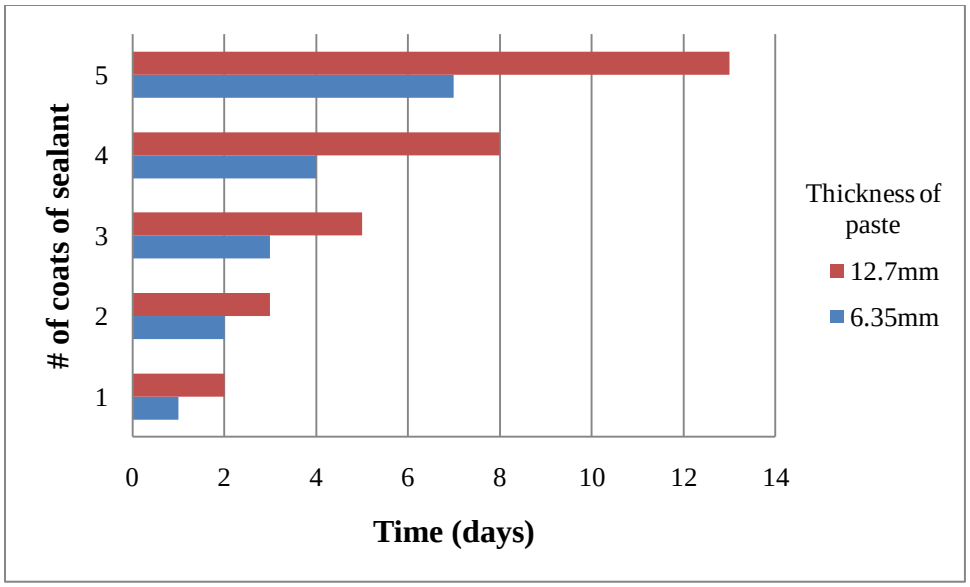


Figure 10: Length of time treatment system retained solvent as a function of paste thickness and number of sealant coats

Figure 10 displays that a 12.70mm thickness of NMTS sealed with 5 coats of sealant retained solvent for almost two weeks. Even if a thicker layer of treatment system would remain moist for a longer time period, its ability to remain on a vertical surface would be compromised. Therefore, the selected parameters of paste for the following experiments included a 12.70mm thickness of NMTS with 5 coats of sealant.

Solvent Evaporation rate

The solvent portion of the treatment system is involved in the removal of PCBs from paint as well as their degradation. Therefore, how the solvent evaporates out of the treatment system is of utmost importance. The following study observed the change in mass as a result of solvent evaporation of unsealed samples of non-metal treatment system.

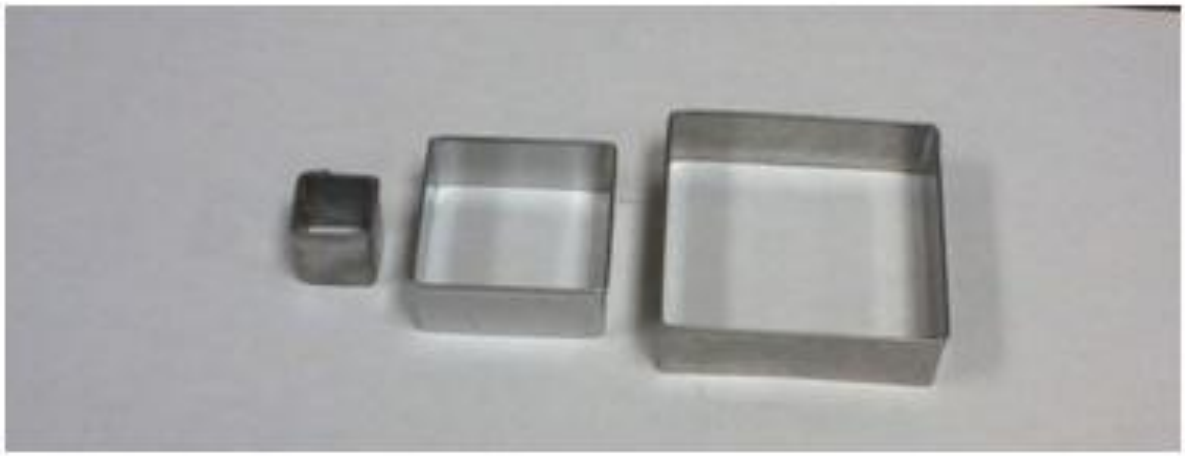


Figure 11: Three molds used to shape treatment system

Three samples of NMTS were molded into square shapes, seen in Figure 11, and placed on individual watch glasses. Each sample had a thickness of 1.6cm with the overall surface area of the NMTS being 69, 39, or 12cm^2. The masses of the samples were measured on a Denver Instrument A160 balance. The change in mass due to the evaporation process was recorded over a 12 hour period. Ethanol is the most volatile liquid in the treatment system and, as a result, is the main component to have evaporated.

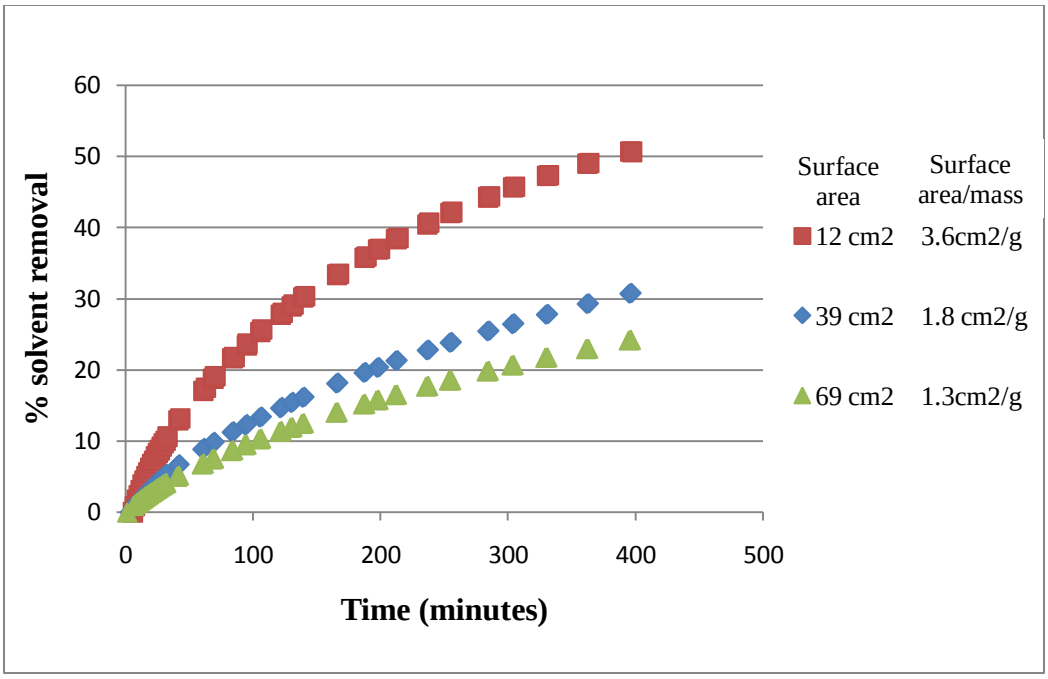


Figure 12: Percent solvent loss over time as a function of surface area

Figure 11 displays the percent solvent loss by mass over time as a function of surface area. The evaporation of the treatment systems is more complex than the evaporation of a pure solvent due to the various components and the relationship between the solvent and the treatment system surface. The treatment system has been designed to retain the solvent like a sponge which is one reason that the sample with the large surface area may have displayed the smallest percent solvent loss by mass. Keeping in mind that all of the surface areas were the same thickness, the solvent in the small surface area sample had a smaller distance to travel to reach the side surfaces for evaporation therefore reporting a larger percent loss of solvent mass. It is expected that the solvent molecules that are furthest away from the surface may be most likely to stay in the system and not evaporate. Though the study does not explain all of the aspects of the complex evaporation process, it establishes a foundation to determine if a large scale application is possible.

PCB removal based on solvent evaporation

The structures that will be remediated through the use of the BTS and NMTS will be on a larger scale than can be replicated in the laboratory. The field use will require longer application times as well as longer sealant times. Solvent evaporation during that time period is inevitable but it is unclear how the loss of solvent would affect the treatment system's ability to remove PCBs. In order to determine the effect that loss of solvent would have on the PCB removal process, NMTS was applied to contaminated paint and sealed at varying times. The longer the NMTS remained un sealed, the more evaporation would take place.

PCB congener 151 was added to Olympic fast hide with ultra semi-gloss white paint. The paint was applied in $2cm^2$ areas on individual pieces of aluminum foil of known masses. After a 24 hour drying period, the mass of the paint was determined from the difference of the combined mass of the paint and aluminum foil and the mass of the plain aluminum foil. Two samples were used as a control to determine the dried paint concentration. NMTS was applied in $3cm^2$ sections to the remaining painted samples. In order to control the amount of solvent evaporation, the samples were sealed with a vinyl polymer sealant at varying times. The first sample was sealed immediately while the others were sealed in thirty minute intervals for a total of three hours. The sealed samples were allowed to sit for three days. After three days, the sealant was peeled away from the paste treatment system and the paste was removed. Excess aluminum foil was cut away from the now exposed painted surface and the treated painted aluminum surface was placed in a 20 ml vial. The paint samples were extracted with 10.0ml of toluene and analyzed for PCBs.

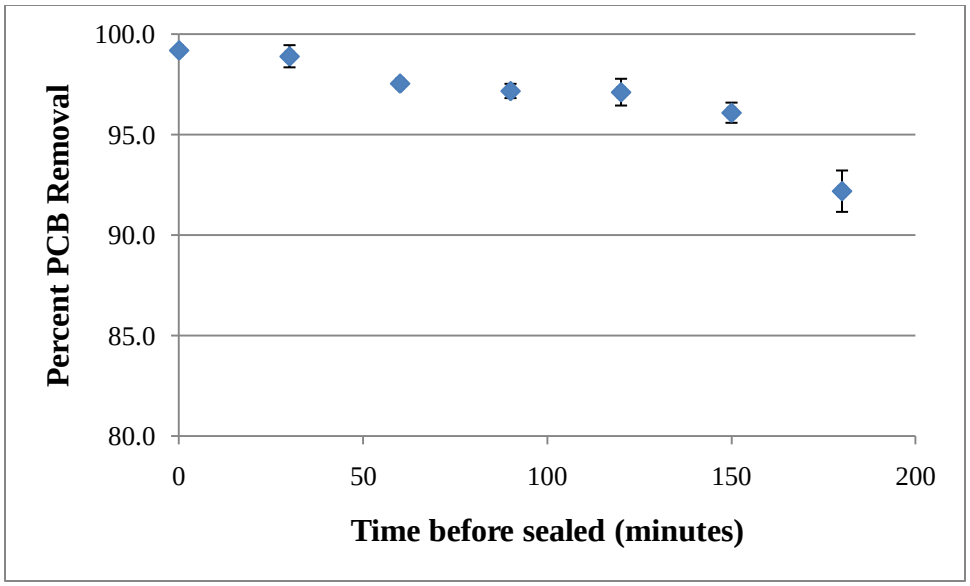


Figure 13: Percent PCB removal as a function of time before the treatment system was sealed

Figure 12 displays the percent PCB removal relative to the time before the sample was sealed with the vinyl sealant. The percentage of the solvent mass that evaporated was calculated according to the data acquired from the same small surface area of 12cm^2 displayed in Figure 11. Figure 12 shows that more than 90 percent of PCBs were removed from contaminated paint even after three hours when 36 percent of the solvent mass had evaporated. Therefore, in a large scale application, the paste is expected to remain effective between the time it takes to apply the treatment system to an entire wall or structure and the time required for the sealing process.

Spiked paint depth test

As discussed previously, it is likely that the porous nature of the concrete was the reason for the large solvent loss during the initial studies. Once the treatment system was modified to retain solvent with the addition of sodium polyacrylate, it was unclear if the PCBs would travel from the painted surface into the concrete material. If this were the case, the concentration of the paint would decrease, but the concentration in the concrete would increase. To determine this, two pieces of concrete block were

painted with PCB-laden latex paint. Approximately 100mg of Aroclor 1254 was added to 0.182 kg of Olympic fast hide with ultra semi gloss white paint. The paint was applied in 3.5cm^2 areas on various sections of each block. A total of three coats of paint were applied with a 24 hour drying period between each coat of paint. Four samples were analyzed to determine the dried paint's PCB concentration. The contaminated paint on one of the concrete blocks was treated with the NMTS and sealed. The other block was left untreated and used as a control. Both concrete blocks were sampled in triplicate after three and seven days. The sampling and analysis included the paint, and concrete concentration. A drill was used to collect samples of concrete at two depths. The first depth was the material between 0mm-7.62mm into the concrete. The second depth tested was between 8mm-18mm into the concrete. The paint and concrete were extracted with 10.0ml of toluene and analyzed for PCBs. The treated piece of painted concrete was compared to the untreated piece and the results are displayed in Table 2.

Table 2: PCB concentrations of paint and concrete over a 7 day treatment period

	3 day		**7 day**	
	Untreated (ppm)	Treated (ppm)	Untreated (ppm)	Treated (ppm)
Paint	242 ± 24.7	65.6 ± 5.30	242 ± 24.7	57.0 ± 10.1
Concrete				
0mm-8mm	3.21 ± 1.98	0.879 ± 0.395	2.41 ± 0.341	0.819 ± 0.234
8mm-18mm	0.125 ± 0.030	0.067 ± 0.005	0.219 ± 0.076	0.111 ± 0.089

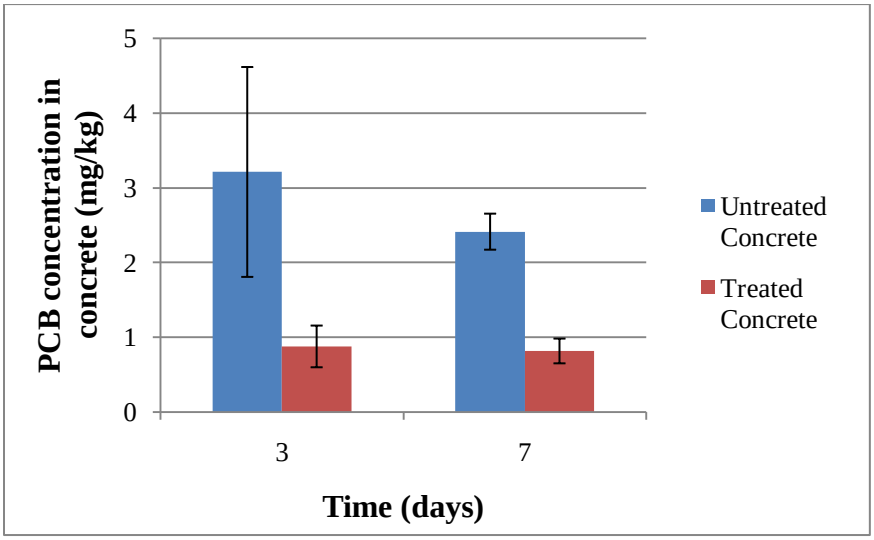


Figure 14: PCB concentration at depth range of 0-8mm

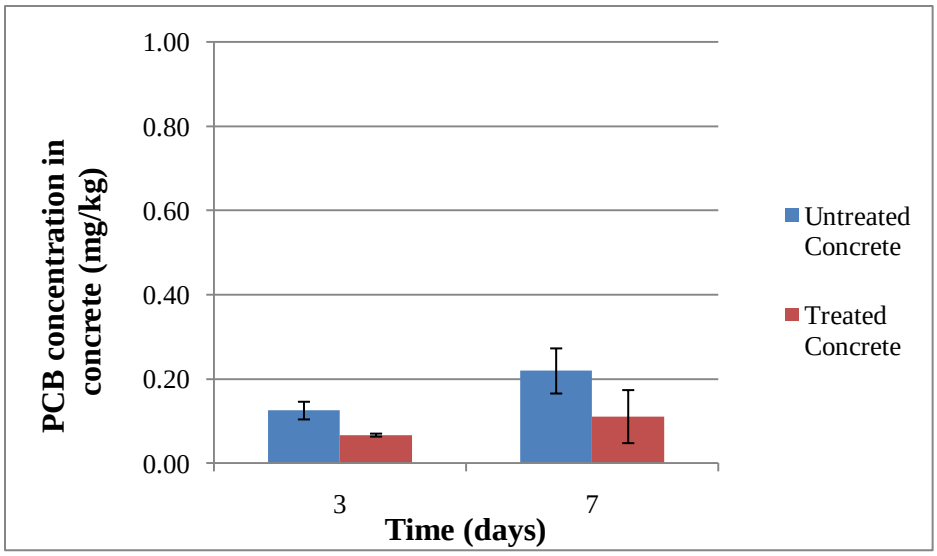


Figure 15: PCB concentration at depth range of 8-18mm

Figures 13 and 14 show that at three days and seven days, there were fewer PCBs in the treated concrete at both depths tested. Therefore, as opposed to the PCBs being pushed further into the concrete, the

NMTS was able to reduce the PCB concentration that was there as a result of the original painting process.

Treatment of field samples

Once the formulation of the treatment system paste was established, its ability to treat samples from an actual field site was analyzed. To do this, samples of painted concrete were received from the DOD site in Wisconsin for analysis. Samples from buildings 6810-36 and 6810-11 were chosen for this study due to the amount of material available and the high PCB concentrations associated with the samples. Each small piece of painted concrete was treated with two sections of a 4cm^2 area of BTS, with a thickness of approximately 12.7mm, and sealed with five coats of vinyl sealant. Due to the small size of the painted concrete samples, a pre-treatment concentration was averaged from a selection of pieces and the treated values were conducted in groups of four. Post-treatment samples were taken on the third and seventh day of treatment, at which time the treated paint was removed from the concrete, extracted in toluene and analyzed by GC-ECD.

Table 3: Removal of PCBs from field site over seven days

Sample	PCB Concentration (mg/kg)			
	Pre-treatment	3 Days	7 Days	Approx. % removal
Bldg 6810-36, 7-A 1	5131 ± 384	539	396	92
Bldg 6810-36, 7-A 2	5131 ± 384	1150	501	90
Bldg 6810-36, 7-A 3	5131 ± 384	1210	480	91
Bldg 6810-36, 7-A 4	5131 ± 384	800	300	94
Bldg 6810-11, 4-A 1	5348 ± 464	979	424	92
Bldg 6810-11, 4-A 2	5348 ± 464	1617	747	86
Bldg 6810-11, 4-A 3	5348 ± 464	1303	425	92
Bldg 6810-11, 4-A 4	5348 ± 464	1500	375	93

Table 3 shows the results after three and seven days. The BTS was able to remove up to 94% of the PCBs in the paint within one week. It is clear from the lower concentrations on day seven compared to day three that the PCB removal process for these locations should exceed three days.

Defining temperature parameters

All of the previous experiments leading up to the field study were done at ambient temperatures. The field study, however, was to occur in Wisconsin in the early spring and would therefore occur in much lower temperatures. The following studies were conducted to explore how temperature affects the treatment system's PCB removal capability.

Two painted metal pieces painted with PCB contaminated paint were acquired from the DOD site in Wisconsin. The pieces were sampled for initial PCB concentrations and then treated in 4 places with NMTS that was applied in a thickness of 12.7mm. Five coats of vinyl sealant were applied to each section and allowed to dry. One metal piece contaminated with Aroclor 1260 was put in a refrigerator with a temperature of 4.5^{o}C while the second piece with Aroclor 1254 was put in a freezer with a temperature of -19^{o}C. The refrigerator and freezer were kept closed throughout the entire treatment process with the exception of when the samples were removed for sampling on day three and were immediately returned. Temperature probes, each with a display outside of the refrigerator or freezer, were used to monitor the temperature of the treatment environments. On the third and seventh day, the sealant and treatment system were removed and the treated paint samples were put in 20ml vials with PTFE lined caps and extracted with toluene. Approximately 0.03g of paint from the metal piece treated at 4.5^{o}C was sampled. Due to the many layers of paint on the second piece, approximately 0.40 g of paint (more than ten times an average amount) from the metal piece treated at -19^{o}C were sampled. One sample from each metal piece was analyzed for initial concentration while samples from day three and day seven were done in duplicate.

Table 4 reports the PCB concentration of the painted metal that was treated at two different temperatures. The treatment system was able to remove PCBs in cool and freezing temperatures. As can be seen in figure 15, the metal piece that was in the cool temperature of 4.5^{o}C had more than 92% of the original PCBs removed over one week while the metal piece in the freezing temperature of -19^{o}C had approximately 70% of the PCBs removed. This implies that temperature may affect the removal

capabilities of the treatment system paste at freezing temperatures. It is also noted that the paint on the metal piece that was in the freezer had more layers of contaminated paint than that of the one on the metal piece in the fridge as indicated by the higher mass of paint that was removed from the same treatment area. More PCBs in the paint as well as more layers of paint the PCBs must travel to go into the treatment paste is a very likely reason why the metal piece in the freezer only achieved 70% removal. In addition, the PCB envelopes of each Aroclor remained characteristic to their initial peak ratios. Therefore, there is no indication that specific congeners are removed better than others at lower temperatures.

Table 4: PCB removal on painted metal related to temperature

	Original concentration (mg/kg)	**3 day concentration (mg/kg)**	**7 day concentration (mg/kg)**
Fridge	1230	197 ± 12.1	84.2 ± 14.7
Freezer	1430	568 ± 38.6	484 ± 67.9

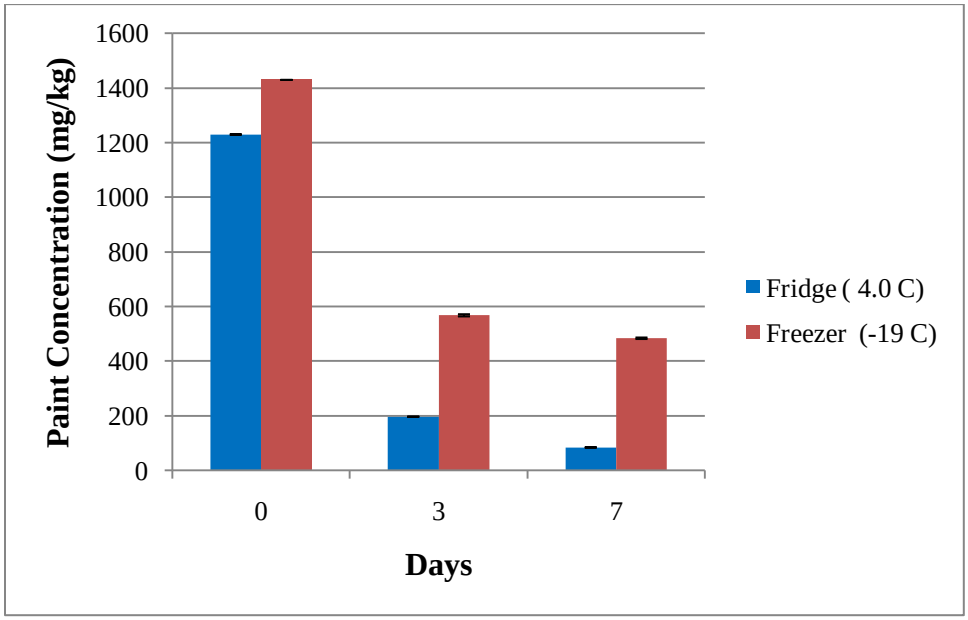


Figure 16: PCB removal on painted concrete related to temperature

A similar study was conducted on painted concrete aimed at replicating parameters close to the field study which was going to involve concrete being treated with BTS. The second study observed PCB removal by the BTS as well as the NMTS. Three pieces of PCB contaminated painted concrete from the DOD site in Wisconsin were acquired and sampled for initial PCB concentrations. Each piece was treated in four sections. Two sections were designated to be treated with the NMTS while the other two sections were designated to be treated with the BTS. The treatment systems were applied 12.7mm thick and sealed with 5 coats of vinyl sealant. Once the treatment system was applied, one concrete piece was placed on a counter at room temperature (24^{o}C), one was placed in a refrigerator (4.5^{o}C), and one was placed in a freezer (-19^{o}C). On the third and seventh day, the sealant and paste were removed and the treated paint was analyzed for PCBs. Approximately 0.05g of paint were placed in 20ml vials with PTFE lined caps and extracted in toluene. Due to the small size of the concrete pieces, each section was sampled once without duplicates.

Table 5: PCB removal on painted concrete related to temperature and type of treatment system

	Non-metal treatment system PCB concentration (mg/Kg)			Bimetallic treatment system PCB concentration (mg/kg)		
	Initial	**3 day**	**7 day**	**Initial**	**3 day**	**7 day**
Freezer (-19^{o}C)	279	39.2	28.9	279	71.28	31
Fridge (4.5^{o}C)	1897	304	89.5	1897	179	159
Room temp (24^{o}C)	1274	396	242	1274	385	336

Table 5 reports the concentrations of the treated concrete exposed to both the NMTS and BTS The treatment systems in the freezing and cool temperatures achieved approximately 90% removal while the room temperature treatment system achieved a little more than 70%.

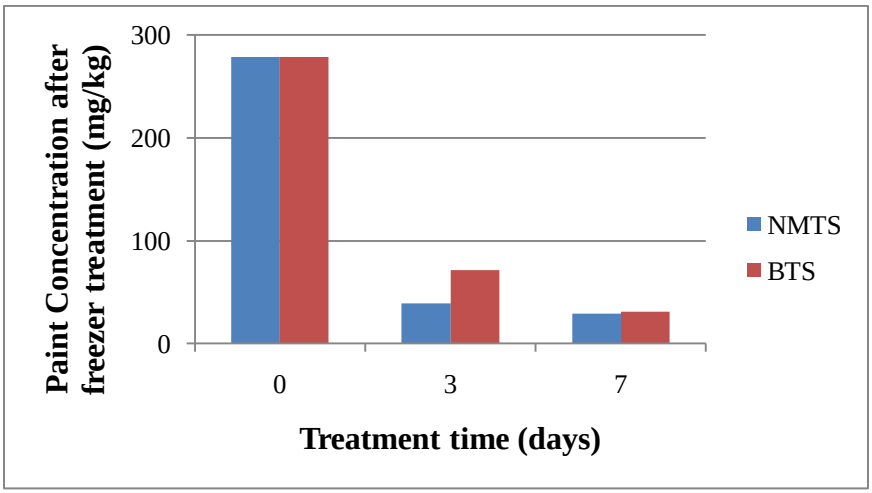


Figure 17: PCB removal at freezing temperature relative to type of treatment system

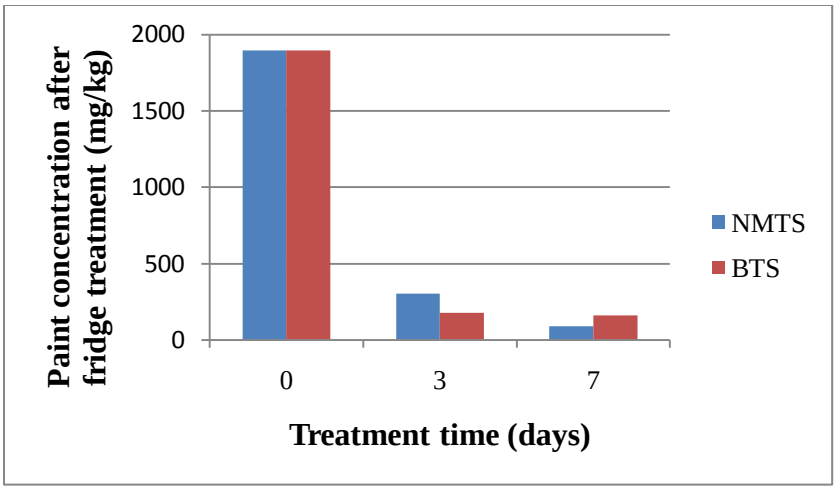


Figure 18: PCB removal at cool temperature relative to type of treatment system

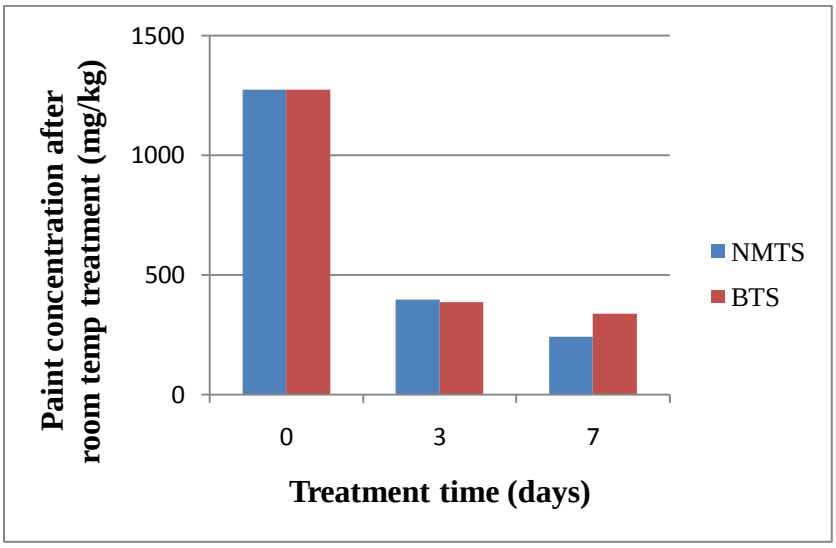


Figure 19: PCB removal at room temperature relative to type of treatment system

Figures 16,17,and 18 display the PCB removal results at freezing, cool, and room temperatures respectively. Given that previous studies on treated concrete have been seen to remove more than 90% PCBs at room temperature, this further indicates that the removal capability of the treatment system depends more on the type and number of layers of paint than on the treatment temperature. In terms of

solvent retention, the cool temperatures may reduce solvent evaporation and allow for more PCB removal.

Treatment Bath

Some of the contaminated materials at industrial field sites may include irregularly shaped machine parts making them difficult to seal the BTS. Therefore, a treatment bath was designed to remediate PCB contaminated painted metal parts. It was envisioned that contaminated metal parts could be submerged into a large drum of treatment paste and left to react on site.

A treatment bath was created by doubling the amount of solvent used to make 1 gallon of NMTS. An irregularly shaped metal piece, shown in Figure 19, was received from the DOD site in Wisconsin and original paint concentrations were sampled from five different locations on the part.

Figure 20: Metal part contaminated with PCB laden paint after initial sampling

The metal piece was submerged in the treatment bath and sealed as seen in Figure 20, although once the photo was taken, the rest of the piece was covered in NMTS. After one week, the metal part was removed and the treatment system was carefully removed from the sampling locations. Due to the vast range in PCB concentrations, the post treatment sampling occurred as close to the pre treatment sampling

as possible. Approximately 0.05g of paint was sampled for PCB concentration. The post treatment sampling was repeated for a final time 10 days later.

Figure 21: Metal part being submerged in NMTS

Table 6: PCB concentrations on painted metal part before and after treatment bath

Sample Location	PCB Concentration (mg/kg)			% removal
	Pre-treatment	7 days	17 days	
A	889	78	30	97
B	774	20	6	97
C	47,722	1,076	200	99
D	1,164	7	16	99
E	8,776	186	41	99

As displayed in Table 6, the treatment bath was able to remove 97-99% of the PCBs originally in the metal part. These initial findings indicate that the dip method is another viable option for onsite remediation. Because this method may have the ability to treat many parts at once, it could be combined with the 'apply and seal' method earlier described to remediate a wide range of contaminated materials at one site.

End of chapter remarks

The preliminary studies described in this chapter have set the stage for a field demonstration utilizing the BTS developed at UCF in conjunction with NASA, KSC. The Mg/Pd bimetal is able to degrade Aroclor mixtures that are found at most PCB-contaminated industrial sites in the United States. The treatment system has been modified with the addition of sodium polyacrylate, a superabsorbent polymer, which allows it to be effective on porous materials, particularly concrete. The system is viscous enough to treat vertical surfaces and is most effective when applied at a thickness of 12.7mm and sealed with five coats of vinyl sealant. Evaporation of the solvent from the surface of the treatment system is slower when more paste is present. Although evaporation does occur, the treatment system is able to remove more than 90% of PCBs in paint even after 36% of the solvent has left. Therefore, it is possible to apply the treatment system to a large structure and still have time to seal it without compromising its removal capabilities. The type and number of layers of paint affects how quickly and easily the PCBs can be removed therefore it is suggested that samples of the contaminated site be tested before the actual field study to determine the necessary length of treatment. For the DOD site used in this paper, the treatment period must extend past three days and preferably past seven. Studies have shown that the treatment system can remove up to 90% of PCBs in paint even in freezing temperatures and the ability to remove PCBs does not seem to be effected if the treatment system contains bimetal. Finally, a treatment bath can be used in addition to the 'apply and seal' method to treat a wide variety of painted structures that may be found at an industrial site. With this method, painted metal parts can be submerged into a drum containing fluid treatment paste and sit in a sealed container, for weeks at a time, as PCBs are removed from the painted surface. All of this information was used in the second part of the research project which involved a scale up field application at a PCB contaminated site in the United States.

CHAPTER FOUR: FIELD APPLICATION

The largest driving force behind the research aimed at developing the BTS paste is the group of PCB-contaminated sites that do not have a cost effective, environmentally friendly option for large scale remediation. In order for the technology to be a viable option for industry, a scaled-up field study was conducted to replicate an authentic remediation process.

Overview of site

Background of site

The site chosen for the field study was a DOD facility located in Sauk County, Wisconsin. The Badger Army Ammunitions Plant, BAAP, was established in 1942. The predominant use of the site was the production of single and double based propellants for cannons, rockets, and small arms ammunition. It was operational intermittently until 1975 when it remained dormant until it was eventually deemed no longer necessary for the nation's defense in 1997. The BAAP had previously been subjected to extensive sampling and analysis by Army contractors to determine the concentration of PCBs and heavy metals. Initial data indicated that Aroclor 1254 and 1260 were the two mixtures of PCBs found on the site. High concentrations of PCBs were found on painted surfaces in the press house building, the nitrating house, the rest house, the roll house, and the staging area. PCB concentrations ranging from 50mg/kg to 40,000mg/kg had been detected on many of the painted structures and equipment including painted tanks and concrete walls. The contamination could be found inside and outside and there was a wide range of paint quality due to weathering.

Sampling and initial concentrations

Site personnel sampled paint from fourteen different locations and sent them to UCF and NASA,KSC to be analyzed for PCBs. The highest levels of PCBs from various sites ranged from 1,068 to 55,219 ppm (mg/kg). These levels were found in the nitrating house, separator house, and the press house buildings.

A member of the UCF/NASA research team visited the site to for additional sampling of materials that were used in laboratory tests to establish the optimal formulations and conditions for the remediation as described in the previous chapter. Samples of the structure material with the paint still attached were necessary and included slices of the painted concrete and painted metal parts. All samples were placed in plastic bags to maintain sample identification and prevent cross contamination. The procedure for paint sampling is described in American Society for Testing and Materials, ASTM, method E1729-05 for field collection of dried paint samples. Paint samples were collected using a cold-scraping procedure with a sharp bladed paint scraper tool followed by a magnet to separate any steel that may have entered the sample batch. Samples that were collected from concrete were shaken on a 60 mesh screen to separate the concrete dust from the paint flakes. Table 7 displays a representation of several initial sample locations, types, and concentrations.

Table 7: Example of building location, sample type, and initial PCB concentration

Sample Location	Sample Type	PCB Concentration (mg/Kg)
Bldg 6810-11 (6-B)	White painted concrete	9540
Bldg 6810-11 (6-E)	White painted concrete	16,450
Bldg 6810-36 (7-K)	White painted concrete	2,125
Bldg 6657-02 (1-A)	Brown painted metal	38,155
Bldg 6815-08 (12-B)	White painted wood	2,435
Staging Area Press	Green painted metal	537

Based on the initial sampling, four locations were chosen for further field testing including press houses 6810-11 and 6810-36, the nitrating tanks 6657-02 and the press staging area.

One of the obstacles of working with weathered field samples is the consistency of the contaminate concentration. The PCB concentrations can vary greatly over a treatment area. Table 8 gives an example of how greatly the PCB levels can differ from point to point. In some areas, the paint can vary up to 7,000ppm (mg/kg) within a matter of feet.

Table 8: Varying PCB concentrations displayed in initial sampling at press houses 6810-11 and 6810-36

Sample # Description/Location	PCB concentration (mg/kg)
Bldg 6810-11 near sample 4 4-A concrete	5,348
Bldg 6810-11 near sample 4 4-B concrete	2,695
Bldg 6810-11 near sample 4 4-C concrete	4,406
Bldg 6810-11 near sample 4 4-D concrete	2,035
Bldg 6810-11 near sample 4 4-E concrete	6,184
Bldg 6810-11 near sample 4 4-G concrete	10,161
Bldg 6810-11 near sample 4 4-H concrete	BDL
Bldg 6810-11 near sample 4 4-I concrete	5,416
Bldg 6810-11 near sample 5 5-A concrete	BDL
Bldg 6810-11 near sample 5 5-B concrete	BDL
Bldg 6810-11 near sample 5 5-C concrete	BDL
Bldg 6810-11 near sample 6 6-A concrete	3,290
Bldg 6810-11 near sample 6 6-B concrete	3,253
Bldg 6810-11 near sample 6 6-C concrete	4,031
Bldg 6810-36 near sample 7 7-A concrete	5,131
Bldg 6810-36 near sample 7 7-B concrete	1,197
Bldg 6810-36 near sample 7 7-B concrete	1,358
Bldg 6810-36 near sample 7 7-C concrete	781
Bldg 6810-36 near sample 7 7-D concrete	1,114
Bldg 6810-36 near sample 7 7-E concrete	1,126
Bldg 6810-36 near sample 7 7-F concrete	2,118
Bldg 6810-36 near sample 7 7-I concrete	1,419
Bldg 6810-36 near sample 7 7-J concrete	646
Bldg 6810-36 near sample 7 7-M concrete	1,067
Bldg 6810-36 near sample 8 8-A concrete	1,661
Bldg 6810-36 near sample 8 8-B concrete	2,630
Bldg 6810-36 near sample 8 8-C concrete	3,780
Bldg 6810-36 near sample 8 8-D concrete	610

For the field demonstration, the paint was sampled before, during and after the treatment period. Treatment of the paint occurred as closely as possible to the initial sample location. This concept can be seen in Figure 21, which is a schematic of the sampling plan for one section of the press house 6810-11 over the entire length of the treatment period.

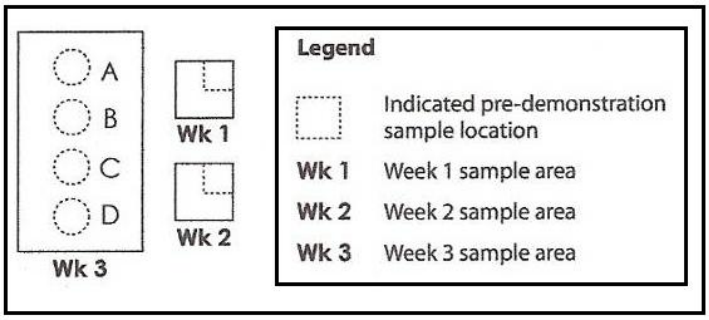


Figure 22: Example of paint sampling layout

Figure22 is a photograph taken of the press house 6810-11 described in Figure 21 after the pre-demonstration samples had been taken. On the right side of the picture, there are slits cut in the wall where concrete samples were taken for laboratory testing.

Figure 23: Post pre-demonstration sampling for paint and concrete

Sites 1&2 press houses 6810-11and 6810-36

The area to be treated in the press houses 6810-11 and 6810-36 were painted interior concrete walls. In each press house, treatment paste was applied to two one-square foot sections that were intended to be sampled after one and two weeks of treatment. A third section with a three- square foot area was intended to be sampled after three weeks. A BTS and NMTS section were both sealed with the vinyl sealant as discussed in the previous chapters. In addition, another BTS section was sealed with a silicon sealant that had been previously studied at NASA, KSC. In total, the three treatment areas were set up to test the two treatment systems as well as the two different sealants. Concrete samples were taken to a depth of 3/8 inches from both press houses before treatment and after three weeks of treatment to determine if the system was transporting the PCBs into the concrete.

Site 3Building 6657-02 nitrating house

The areas to be treated in the nitrating house were two painted metal nitrating tanks located inside the building. The larger of the two tanks was sampled in three treatment areas, two on the side and one on the lid. The smaller of the two tanks was sampled with one treatment area. As in the press houses, the nitrating house was also intended to test the two treatment systems with the two sealants

Site 4 Staging area

The staging area was the site of five painted metal presses that were located outside. One treatment area was chosen for each press and the section of the press that was treated varied for each structure. BTS sealed with the vinyl sealant was the only technology chosen to be used at this site. The treatment system and paint were sampled at the one week and three week time points.

Description of treatment procedure

Application of treatment system

The treatment systems were applied to the test sections by troweling on it as seen in figure 23. Two types of sealants were applied on top of the BTS and NMTS. The vinyl sealant was sprayed on with a cartridge spray gun while the silicon sealant was applied using a commercial spray gun shown in Figure 24.

(a) **(b)**

Figure 24: BTS applied by troweling prior to being sealed a) Press house 6810-36 b) Staging area

(a) **(b)**

Figure 25: Press house 6810-11 a) Vinyl sealant being applied by cartridge spray gun b) Silicon sealant being applied by commercial spray gun

The day after the treatment application, both sealants had small cracks that may have been due to the cold weather, which was below 0^{o}C. To seal the cracks in the vinyl sealant, additional vinyl was sprayed on with a commercial aerosol can. Additional silicon sealant was applied using a brush to seal cracks in the silicon sealant. This was repeated everyday if cracks were found until the first week had passed and the one week samples were taken.

Treatment of press house 6810-11

Three treatment areas were set up in press house 6810-11 as displayed in Figure 25. The first section contained Mg/Pd and was sealed with a vinyl polymer. The second section contained Mg/Pd and was sealed with a silicon polymer. The third section contained no active metal and was sealed with a vinyl polymer.

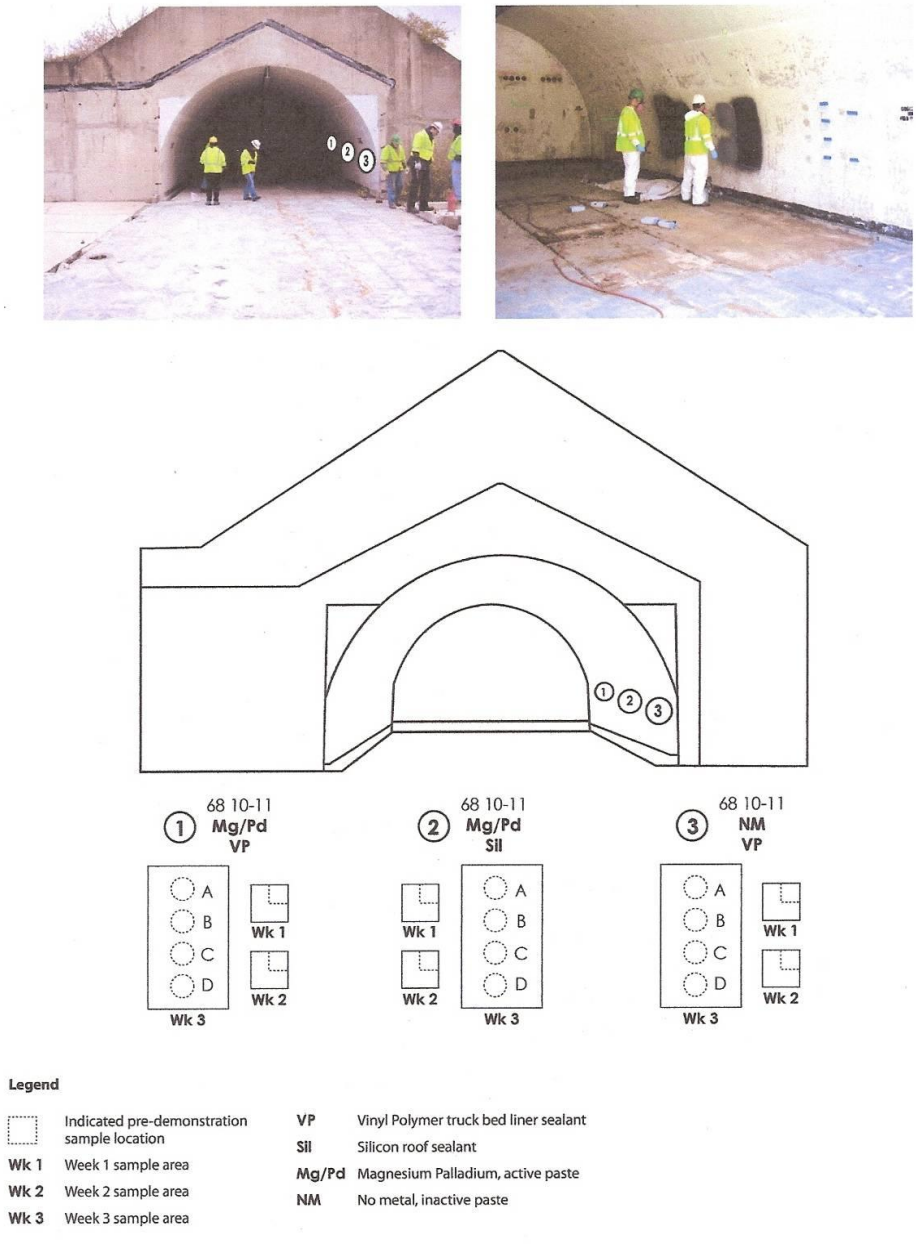


Figure 26: Application plan for press house 6810-11

Figures 26, 27, and 28 are photographs of the three treatments areas in press house 6810-11 three days after application. At this point, all of the treatment areas are intact and all of the cracks are sealed.

Figure 27: Press house 6810-11 NMTS with vinyl sealant

Figure 28: Press house 6810-11 BTS with silicon sealant

Figure 29: Press house 6810-11 BTS with vinyl sealant

Figures 29, 30, and 31 are close up photographs of the treatment paste after the seal was removed one week after initial application. Figure 29 shows the white NMTS surrounded by the black vinyl sealant. Figures 30 and 31 show the grey BTS with the grey silicon sealant and black vinyl sealant respectively.

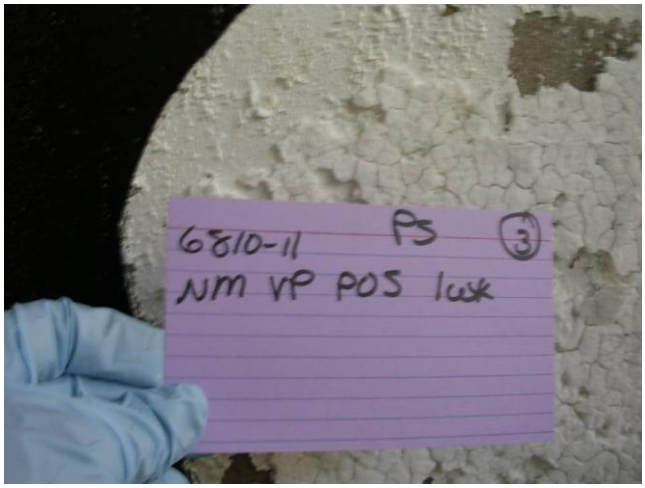


Figure 30: Press house 8610-11 one week sample of NMTS with vinyl sealant

Figure 31: Press house 6810-11 one week sample of BTS with silicon sealant

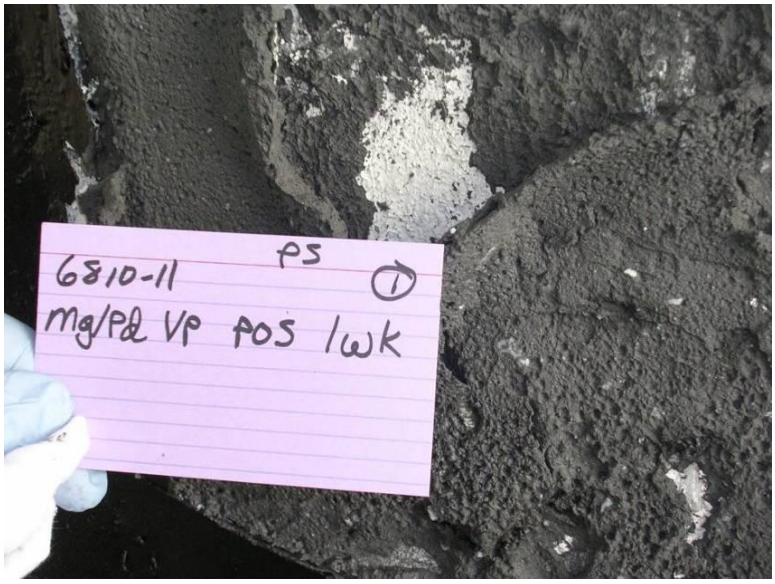
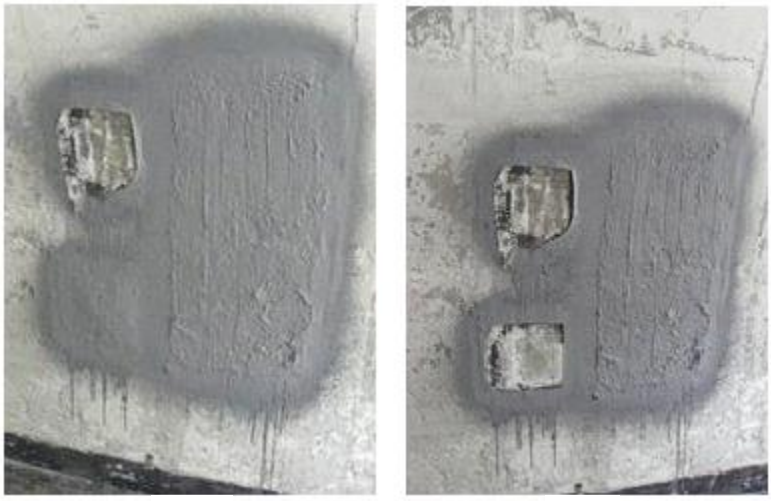


Figure 32: Press house 6810-11 one week sample of BTS with vinyl sealant

The painted concrete in the press houses was extremely powdery which led to some setbacks. During the treatment period, there were a few instances where the vinyl sealant was compromised and broke loose

from the structure. Figure 32 shows the BTS sealed with the silicon sealant before and after the two week sampling. As pictured, the bottom square was sampled as it was intended. The BTS sealed with the vinyl sealant, however, broke loose before week two in the area intended for the three week sampling as seen in figure 33. Therefore, it was decided to sample this location as the two week sample and leave the still completely sealed bottom square to be sampled on week three.

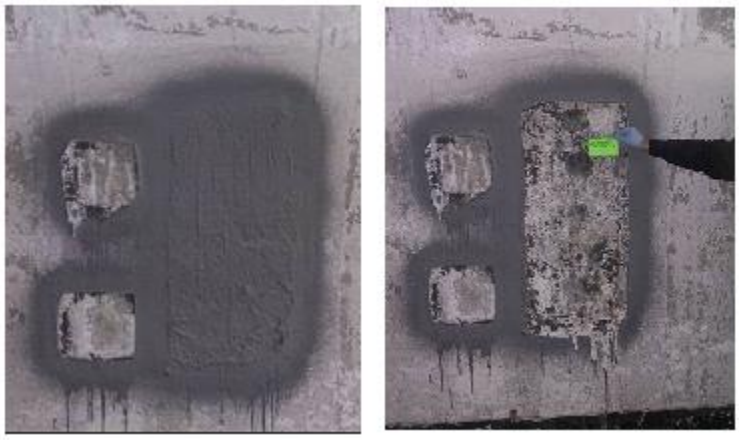


(a) **(b)**

Figure 33: 6810-11 BTS with silicon sealant a) prior two week sampling b) after two week sampling as planned

Figure 34: BTS with compromised vinyl sealant prior to week two sampling

A similar problem occurred again with the vinyl sealant between week two and week three. Figure 34 shows the BTS with the silicon sealant as intended before and after week three sampling. This time, it was the NMTS sealed with the vinyl sealant that was compromised, as seen in figure 35.



(a) **(b)**

Figure 35: 6810-11 BTS with silicon sealant a) prior to three week sampling b) after three week sampling as planned

Figure 36: NMTS with compromised vinyl sealant (large section) prior to week three sampling

The most likely reason for this issue is the inability for the treatment system to adhere to the vertical surface due to its powdery nature. The edges of the sealant remained intact as it was the middle of the sealant that ripped. It appears that the treatment system slid down the wall and eventually broke the sealant.

Concrete samples were taken after three weeks as seen in figure 36. This was done on locations from the NMTS area sealed with vinyl sealant, seen in figure 36, as well as from the BTS area sealed with silicon sealant.

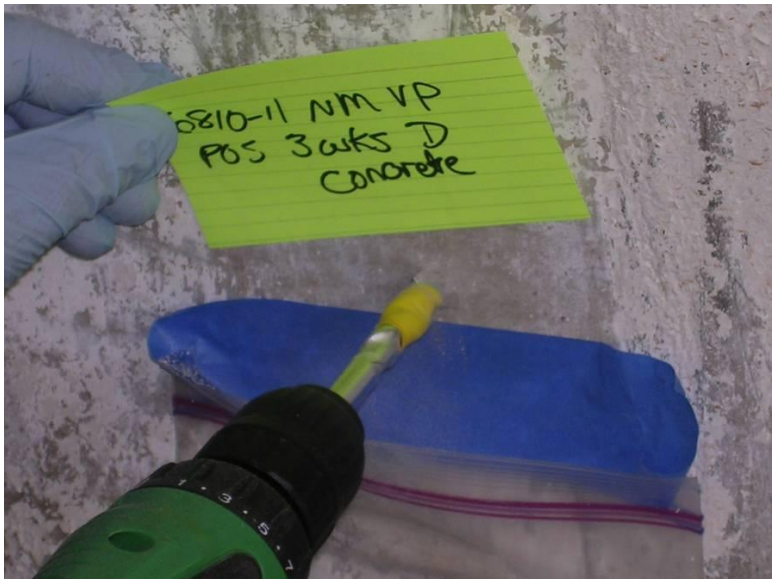


Figure 37: 6810-11 concrete being sampled at NMTS with vinyl sealant area

Press house 6810-36

Three treatment areas were set up in press house 6810-36 as displayed in Figure 37. The first section contained no active metal and was sealed with a vinyl polymer. The second section contained Mg/Pd and was sealed with a vinyl polymer. The third section contained Mg/Pd and was sealed with a silicon polymer.

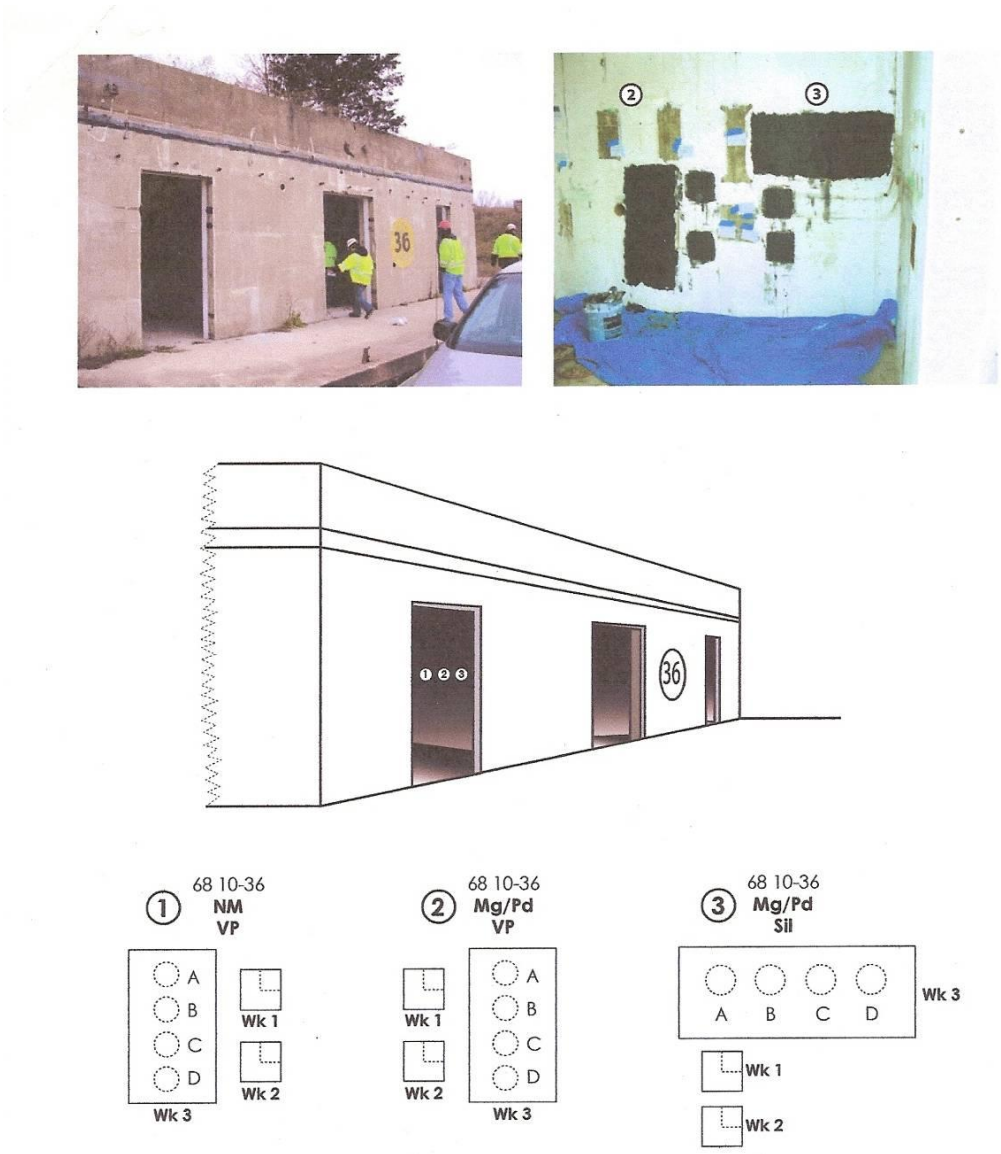


Figure 38: Application plan for press house 6810-36

The paint in press house 6810-36 was reported to be even more powdery and flaky and was subject to the same difficulties of 6810-11. Because of this, it was difficult to get the treatment system and sealant to adhere to the wall. Within the first three days, the vinyl polymer remained intact as seen in figure 38.

(a) **(b)**

Figure 39: 6810-36 a) NMTS sealed with vinyl polymer b) BTS sealed with vinyl polymer

However, the silicon sealant that was intended to protect the third week sample of BTS began to fail immediately and was therefore sampled at the end of one week instead. This is shown in Figure 39

Figure 40: 6810-36 BTS with compromised silicon sealant

After the first week of treatment, the BTS sealed with the vinyl polymer remained intact while the NMTS sealed with the vinyl polymer had broken loose at the three foot treatment section. Therefore the BTS sealed with the vinyl sealant was the only area sampled as intended. The other two areas were sampled in the three foot section for the first week. The sealant integrity did not change between week one and week two. Figure 40 shows the BTS samples with vinyl sealant sampled after two days leaving the large area for week three as anticipated. Figure 41, however, displays the large sections that were sampled after week one as well as the small square sampled at week two for areas containing BTS with silicon and NMTS with vinyl.

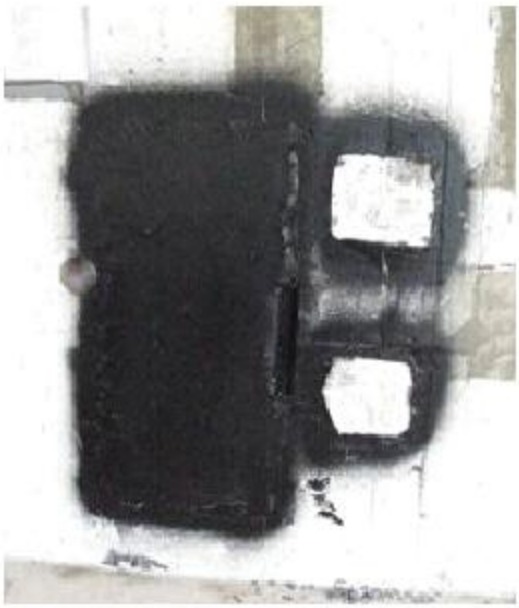


Figure 41: 6810-36 BTS with vinyl sealant after two week sampling as planned

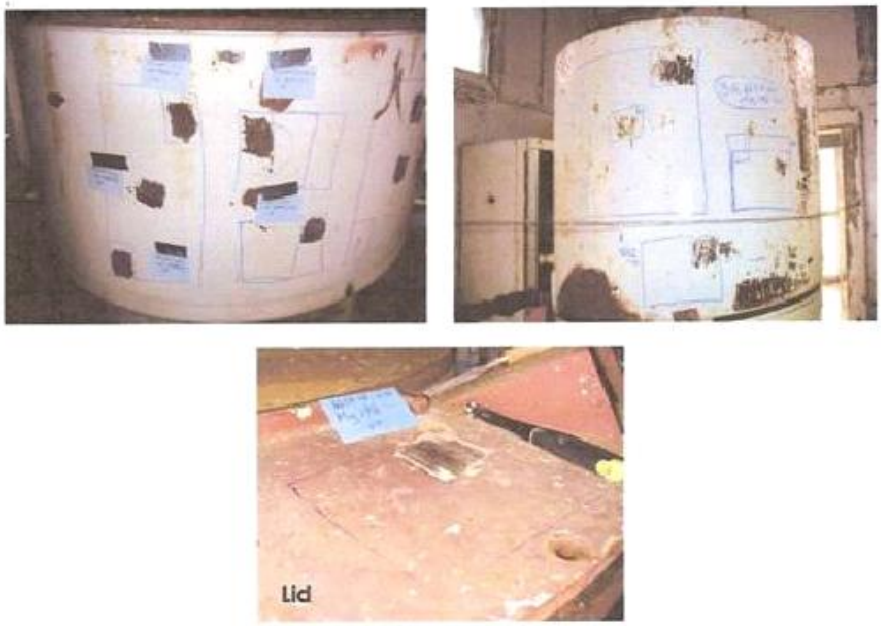
(a) **(b)**

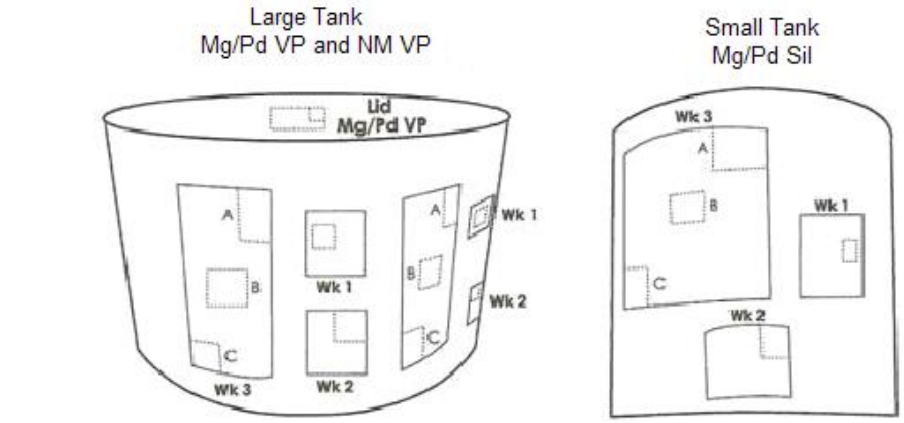
Figure 42: 6810-36 two week sampling of a) BTS with silicon sealant b) NMTS with vinyl sealant

The remaining paint and paste samples were acquired at the end of three weeks at which time concrete samples were taken from behind the BTS with the silicon sealant and BTS with vinyl sealant.

Nitrating House 6657-02

Three treatment areas and an additional treatment section on the lid of a tank were set up in nitrating house 6657-02 as displayed in Figure 42. The large tank was treated with BTS and NMTS sealed with the vinyl sealant. The small tank was treated with BTS sealed with the silicon sealant





Legend

	Indicated pre-demonstration sample location	VP	Vinyl Polymer truck bed liner sealant
Wk 1	Week 1 sample area	Sil	Silicon roof sealant
Wk 2	Week 2 sample area	Mg/Pd	Magnesium Palladium, active paste
Wk 3	Week 3 sample area	NM	No metal, inactive paste

Figure 43: Application plan for nitrating house 6657-02

Both the vinyl and silicon sealant remained intact for the entire three weeks during the treatment of the metal tanks in the nitrating house. Figure 43 shows the large tank after the treatment systems were sealed including the treatment section on the lid. As each sampling took place, the sealant was peeled away to expose the treatment system and the paint as seen in Figure 44. The small tank, displayed in Figure 45, was sampled in the same manner.

(a) **(b)**

Figure 44: 6657-02 a) Large tank sealed with vinyl sealant b) Lid on large tank

(a) **(b)**

Figure 45: 6657-02 One week sampling a) NMTS with vinyl sealant b) BTS with vinyl sealant

(a) **(b)**

Figure 46: 6657-02 NMTS sealed with silicon on small tank a) after week two sampling b) during week one sampling

Staging area

Five metal presses were chosen to be treated; all with BTS sealed with vinyl sealant. Sampling occurred exclusively at the one week and three week time periods. Each treatment area remained sealed with no cracking or separation from the presses. Figure 46 shows the one week and three week samples during the treatment period for press 4 and press 15. In Figure 47, the integrity of the treatment system and sealant is displayed before and after sampling on week one.

(a) **(b)**

Figure 47: BTS sealed with vinyl sealant at staging area a) press 4 b) press 15

(a) **(b)**

Figure 48: BTS sealed with vinyl sealant a) prior to one week sampling b) during one week sampling

Weekly breakdown of concentrations

The following sections report PCB concentrations for the various samples obtained throughout the treatment period broken down by location. Once the samples were received at the UCF laboratory, an effort was made to homogenize the paint chips and analyze representative samples. The data presented in

the tables displays detailed information including specific areas like the large treatment sections with areas labeled A,B,C and D. The data presented in the bar graphs represents an average of all of the samples analyzed and is intended to aid in understanding the overall effect of the treatment process. All of the samples labeled "na" are not available due to mislabeling at the treatment sites, not receiving the sample, or as a result of the sample being accidently compromised.

Press house 6810-11

The changes in paint concentration over the treatment period are displayed in Table 9. All of the samples, except for paint from NM VP 3ft B, were analyzed in duplicate.

Table 9: Press house 6810-11 PCB concentrations in paint over a treatment period of three weeks

Location Name	Treatment time (weeks)	Pre average PCB conc. (mg/kg)	Post average PCB conc. (mg/kg)
NM VP 1 ft	1	1888 ± 90.0	95.5 ± 4.95
NM VP 1 ft	2	3262 ± 881	167 ± 38.2
NM VP 3 ft A	3	2138 ± 201	na
NM VP 3 ft B	3	1782	223 ± 32.3
NM VP 3 ft C	3	2082 ± 40.0	113 ± 16.2
NM VP 3 ft D	3	2192 ± 140	178 ± 6.65
Mg/Pd Sil 1 ft	1	2111 ± 60.0	93.3 ± 5.69
Mg/Pd Sil 1 ft	2	1420 ± 110	220 ± 2.83
Mg/Pd Sil 3 ft A	3	2074 ± 329	276 ± 8.32
Mg/Pd Sil 3 ft B	3	2199 ± 30.4	216 ± 10.7
Mg/Pd Sil 3 ft C	3	1942 ± 202	137 ± 12.2
Mg/Pd Sil 3 ft D	3	1853 ± 47.3	355 ± 13.8
Mg/Pd VP 1 ft	1	2793 ± 363	185 ± 13.4
Mg/Pd VP 3 ft A	2	na	194 ± 5.50
Mg/Pd VP 3 ft B	2	2550 ± 98.2	na
Mg/Pd VP 3 ft C	2	2777 ± 177	291 ± 28.0
Mg/Pd VP 3 ft D	2	2308 ± 8.48	168 ± 14.1
Mg/Pd VP 1 ft	3	2862 ± 989	251 ± 8.74

Figure 48 displays the relative concentrations of all three areas over the treatment period. It is observed that the largest removal of PCBs occurred within the first week for all of the treatment areas. PCB concentrations measured in the paint treated with NMTS with the vinyl sealant and the Mg/Pd with the silicon sealant increased between week one and week two. This may be due to the variability of contamination from one spot to another in the field samples. This may also be due to PCBs being drawn out of the concrete and into the paint before traveling into the treatment system. After week one, however, all three areas remain relatively constant.

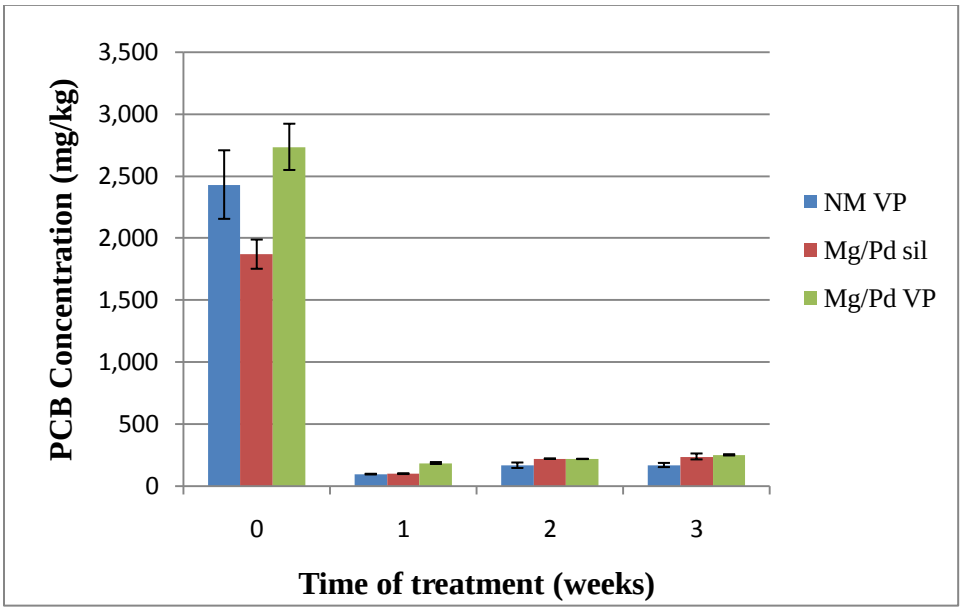


Figure 49: Press house 6810 PCB in paint concentration over three weeks. The three foot sections were averaged

Table 10 and Figure 49 display the PCB concentrations in the different treatment systems. The longer the treatment system remained on the painted surface, the more PCBs were detected. The PCB concentration in the NMTS is significantly higher than that of either of the BTS samples after three weeks. This will be discussed later in the chapter.

Table 10: Press house 6810-11 PCB concentrations in treatment paste over the treatment period of three weeks

Location Name	Treatment time (weeks)	Post average PCB conc. (mg/kg)
NM VP	1	32.3 ± 0.577
NM VP	2	56.0 ± 12.5
NM VP	3	162 ± 60.1
Mg/Pd Sil	1	13.3 ± 7.23
Mg/Pd Sil	2	23.0 ± 2.00
Mg/Pd Sil	3	61.3 ± 6.42
Mg/Pd VP	1	22.7 ± 2.08
Mg/Pd VP	2	36.2 ± 10.4
Mg/Pd VP	3	63.0 ± 18.5

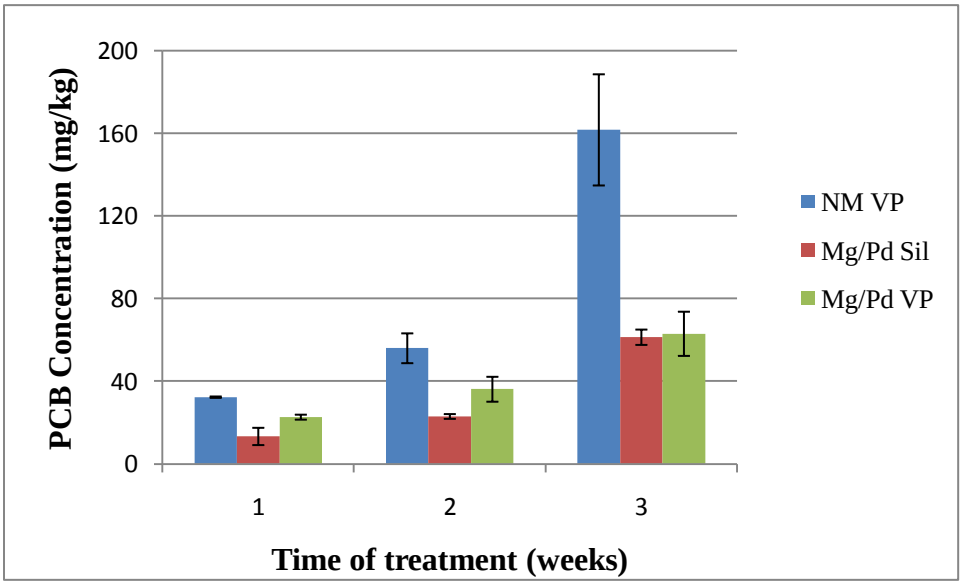


Figure 50: Press house 6810-11 PCB in treatment paste concentration over three weeks

Press house 6810-36

The changes in paint concentration over the treatment period are displayed in Table 11. All of the samples, except for paint from Mg/Pd Sil 3 ft A and B, were analyzed in duplicate. As can be seen in

Figure 50, like press house 6810-11, the largest removal of PCBs occurred within the first week. The majority of the paint samples treated with BTS sealed with the vinyl sealant were reduced to below the EPA action limit of 50ppm (mg/kg).

Table 11: Press house 6810-36 PCB concentrations in paint over the treatment period of three weeks

Location Name	Treatment time (weeks)	Pre average PCB conc. (mg/kg)	Post average PCB conc. (mg/kg)
NM VP 3 ft A	1	402 ± 16.3	na
NM VP 3 ft D	1	729 ±21.9	98.0 ± 4.10
NM VP 1 ft	2	911 ± 15.0	45.3 ± 2.08
NM VP 1 ft	3	815 ± 49.3	110 ± 7.07
Mg/Pd Sil 3 ft A	1	854 ± 0.707	82
Mg/Pd Sil 3 ft B	1	862 ± 64.3	112
Mg/Pd Sil 3 ft C	1	637 ± 66.4	67.5 ± 2.12
Mg/Pd Sil 3 ft D	1	801 ±84.9	na
Mg/Pd Sil 1 ft	2	812 ± 38.0	83.3 ± 7.37
Mg/Pd Sil 1 ft	3	815 ± 35.0	141 ± 12.0
Mg/Pd VP 1 ft	1	595 ± 35.4	40.0 ± 0.010
Mg/Pd VP 1 ft	2	547 ± 35.1	37.3 ± 4.72
Mg/Pd VP 1 ft A	3	525 ± 24.0	55.3 ± 0.577
Mg/Pd VP 1 ft B	3	na	27.0 ± 1.73
Mg/Pd VP 1 ft C	3	394 ± 10.6	48.3 ± 1.73
Mg/Pd VP 1 ft D	3	706 ± 24.7	26.5 ± 2.12

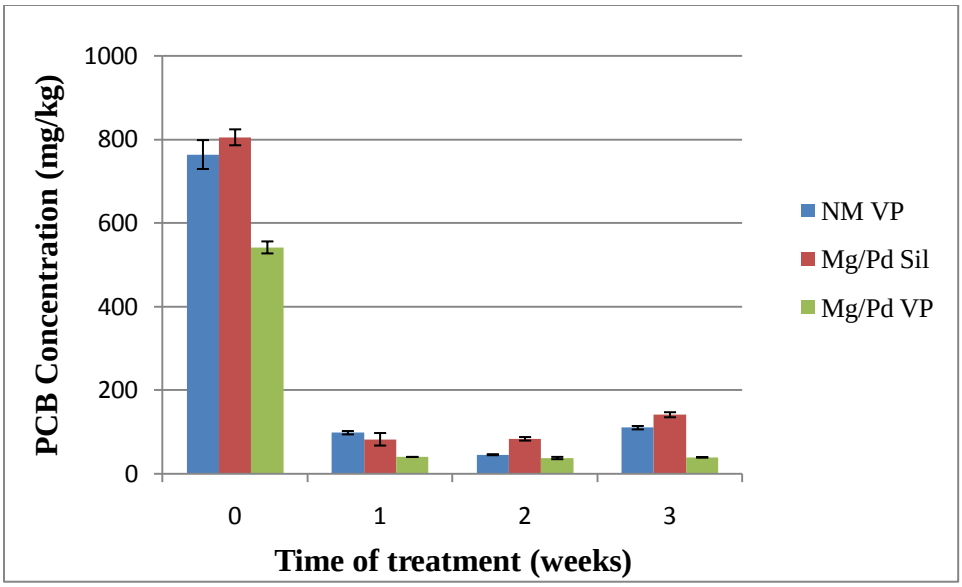


Figure 51: Press house 6810-36 PCB in paint concentration over three weeks

Table 12 and Figure 51 display the PCB concentrations of the three treatment systems over the three weeks. Similar to press house 6810-11, the NMTS sealed with the vinyl polymer has a significantly larger concentration than the BTS. In fact, the PCB concentration in the BTS seems to remain relatively constant after the first week.

Table 12: Press house 6810-36 PCB concentrations in treatment paste over the treatment period of three weeks

Location Name	Treatment time (weeks)	Post average PCB conc. (mg/kg)
NM VP 3 ft	1	56.0 ± 4.24
NM VP 1 ft	2	95.3 ± 18.1
NM VP 1 ft	3	152 ± 7.78
Mg/Pd Sil 3ft	1	43.0 ±13.5
Mg/Pd Sil 1ft	2	25.3 ± 12.2
Mg/Pd Sil 1ft	3	50.0 ± 11.3
Mg/Pd VP 1 ft	1	40.3 ± 6.11
Mg/Pd VP 1 ft	2	39.3 ± 17.0
Mg/Pd VP 3 ft	3	34.3 ± 17.0

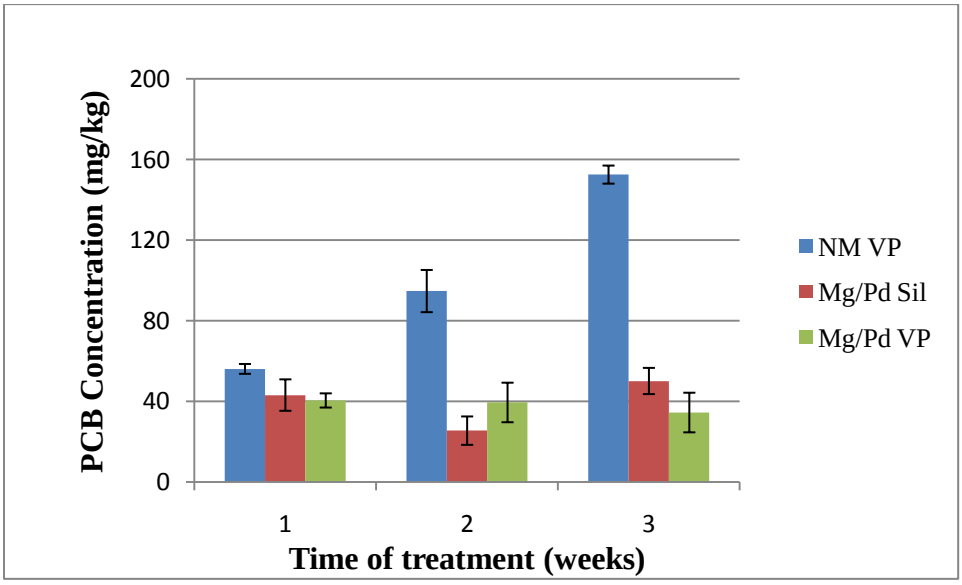


Figure 52: Press house 6810-36 PCB in treatment paste concentration over three weeks

Concrete samples from press house 6810-11 and press house 6810-36 are displayed in Tables 13 and 14 respectively. The initial PCB concentrations of the concrete ranged from approximately 30ppm to

140ppm. After the painted wall was treated with the NMTS or BTS, the PCB concentration at each area sampled decreased, implying that the PCBs are not being transferred into the surrounding material.

Table 13: Press house 6810-11 PCB concentration in concrete before and after the treatment period

Location Name	Treatment time (weeks)	Pre average PCB conc. (mg/kg)	Post average PCB conc. (mg/kg)
NM VP 3 ft concrete A	3	47.6 ± 6.43	41.6 ± 2.08
NM VP 3 ft concrete D	3	34.7 ± 4.16	24.3 ± 2.87
Mg/Pd sil 3 ft concrete	3	29.7 ± 5.69	13.3 ± 0.578

Table 14: Press house 6810-36 PCB concentration in concrete before and after treatment period

Location Name	Treatment time (weeks)	Pre average PCB conc. (mg/kg)	Post average PCB conc. (mg/kg)
Mg/Pd Sil 1 ft	3	139 ± 49.0	18.3 ± 3.20
Mg/Pd VP	3	58.5 ± 18.0	20 .0 ± 10.2

Nitrating House 6857-02

The concentrations from the painted metal tanks in the nitrating house are displayed in Table 15. All of the samples, except for paint from Mg/Pd Sil 1 ft C and Mg/Pd VP 1 ft A, B, & C were analyzed in duplicate.

Table 15: Nitrating house 6857-02 PCB concentrations in paint over the treatment period of three weeks

Location Name	Treatment time (weeks)	Pre average PCB conc. (mg/kg)	Post average PCB conc. (mg/kg)
NM VP 1 ft	1	42660 ± 2690	19824 ± 1205
NM VP 1 ft	2	33263 ± 1901	14016 ± 415
NM VP 3 ft A	3	33879 ± 1951	6576 ± 1697
NM VP 3 ft B	3	28051 ± 11981	11503 ± 1232
NM VP 3 ft C	3	36055 ± 4471	16907 ± 545
Mg/Pd Sil 3 ft	1	20089 ± 1038	8687 ± 434
Mg/Pd Sil 1 ft	2	28970 ± 6176	12585 ± 1835
Mg/Pd Sil 1 ft A	3	35303 ± 2926	21535 ± 2120
Mg/Pd Sil 1 ft B	3	35532 ± 3429	15166 ± 1037
Mg/Pd Sil 1 ft C	3	27548 ± 3618	14209
Mg/Pd VP 1 ft A	1	20403 ± 1028	8666
Mg/Pd VP 1 ft B	1	19893 ± 288	9131
Mg/Pd VP 1 ft C	1	19970 ± 1798	8263
Mg/Pd VP 1 ft	2	40306 ± 13497	15825 ±2875
Mg/Pd VP 3 ft	3	32794 ± 3325	16864 ± 1120
Mg/Pd VP lid	3	37154 ± 4304	10605 ± 2947

Figure 52 displays the average PCB concentration in paint over three weeks. The treatment area on the lid of the large tank was only sampled on week three. The nitrating house differed from the press houses not only due to its metal surface but also due to the extremely high PCB concentrations in the paint. It was at this location that there was the largest mass flux of PCBs even though the percentage of PCBs removed from the painted tanks is well below what was seen in laboratory studies. This may be due to the type of paint or number of layers painted on the surface as described in Chapter 3. These types of structures may be appropriate candidates for a reapplication of the treatment system.

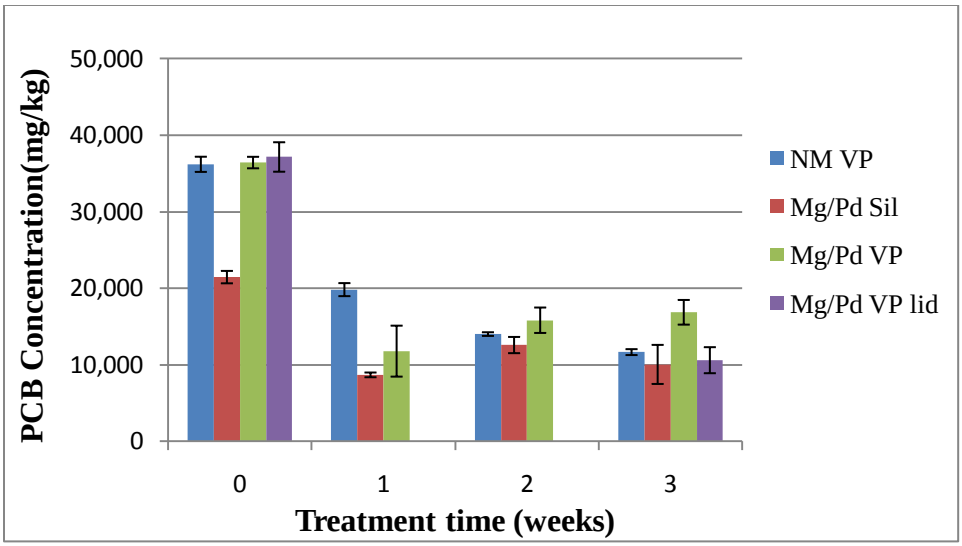


Figure 53: Nitrating house 6857-02 PCB concentration in paint over three weeks. Sample Mg/Pd VP lid was only sampled after the third week.

Table 16 and Figure 53 display the PCB concentrations for the treatment system paste from the nitrating house. These concentrations were also notably high.

Table 16: Nitrating house 6857-02 PCB concentrations in treatment paste over the treatment period of three weeks

Location Name	Treatment time (weeks)	Post average PCB conc. (mg/kg)
NM VP large tank 1ft	1	298 ± 60.1
NM VP large tank 1ft	2	1554 ± 206
NM VP large tank 3ft	3	1781 ±386
Mg/Pd Sil small tank 3 ft	1	688 ± 163
Mg/Pd Sil small tank 1 ft	2	4490 ± 243
Mg/Pd Sil small tank 1 ft	3	716 ±104
Mg/Pd VP large tank 1 ft	1	179 ± 82.7
Mg/Pd VP large tank 1 ft	2	464 ± 68.7
Mg/Pd VP large tank 3 ft	3	na
Mg/Pd VP large tank 1ft lid	3	141 ± 34.0

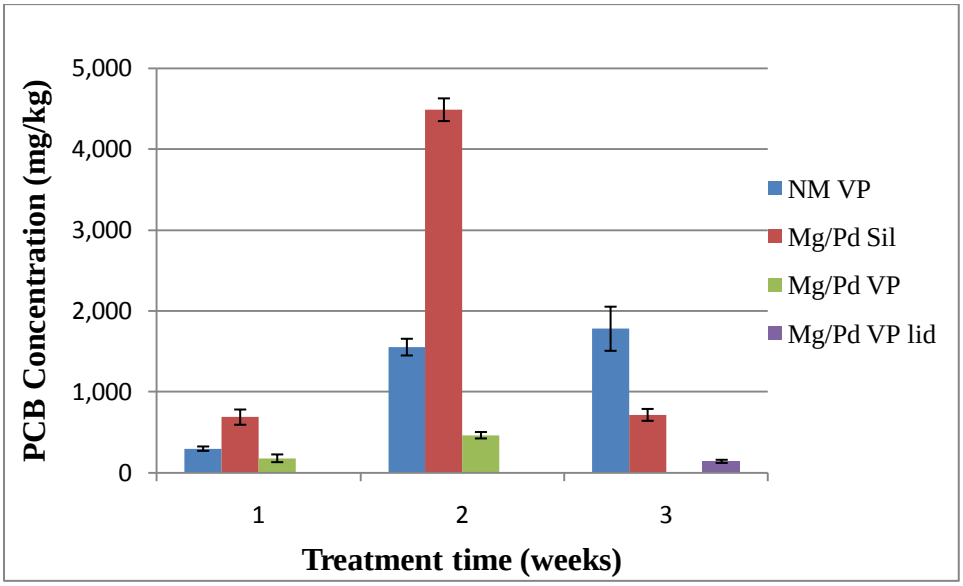


Figure 54: Nitrating house 6857-02 PCB in treatment paste concentration over three weeks. Samples from Mg/Pd VP were never received for analysis.

The NMTS and BTS sealed with the vinyl sealant follow the trends set by the samples in the press houses. The PCB concentration of the week two BTS sealed with the silicon sealant, however, is 6 times higher than the week one or week two. The most likely cause for this spike is an infiltration of paint chips even though special care was taken to not incorporate the paint with the treatment system during the removal process. Paint chips were found in the BTS during laboratory sampling and large pieces were removed with tweezers, but it is possible that some paint chips remained in the BTS during extraction and analysis. Due to the high concentration of the paint, any paint chip that ended up in the treatment system would greatly increase the sample's concentration.

Staging Area

The initial concentrations at the staging area were the lowest of all of the sample locations. Many of the presses were already under the action limit of 50ppm. Table 17 and Figure 54 display the PCB concentrations after the first and third weeks, keeping in mind that no sampling was done at the end of week two. Many of the samples from the staging area were below the detection limit (BDL). The largest decline in PCB concentration occurred after the first week of treatment with the BTS.

Table 17: Staging area PCB concentrations in paint over the treatment period of three weeks

Location Name	Treatment time (weeks)	Pre average PCB conc. (mg/kg)	Post average PCB conc. (mg/kg)
Mg/Pd VP Press # 4	1	93 ±11.3	13.3 ± 3.51
Mg/Pd VP Press # 4	3	na	6.50 ± 0.707
Mg/Pd VP Press # 12	1	160 ± 5.66	3.00 ± 0.10
Mg/Pd VP Press # 12	3	na	3.50 ± 0.707
Mg/Pd Press # 14	1	8.50 ± 0.707	2.33 ±0.577
Mg/Pd Press # 14	3	na	12.5 ± 0.707
Mg/Pd Press # 15	1	5.50 ± 3.53	BDL
Mg/Pd Press # 15	3	na	BDL
Mg/Pd Press # 36	1	BDL	BDL
Mg/Pd Press # 36	3	na	BDL

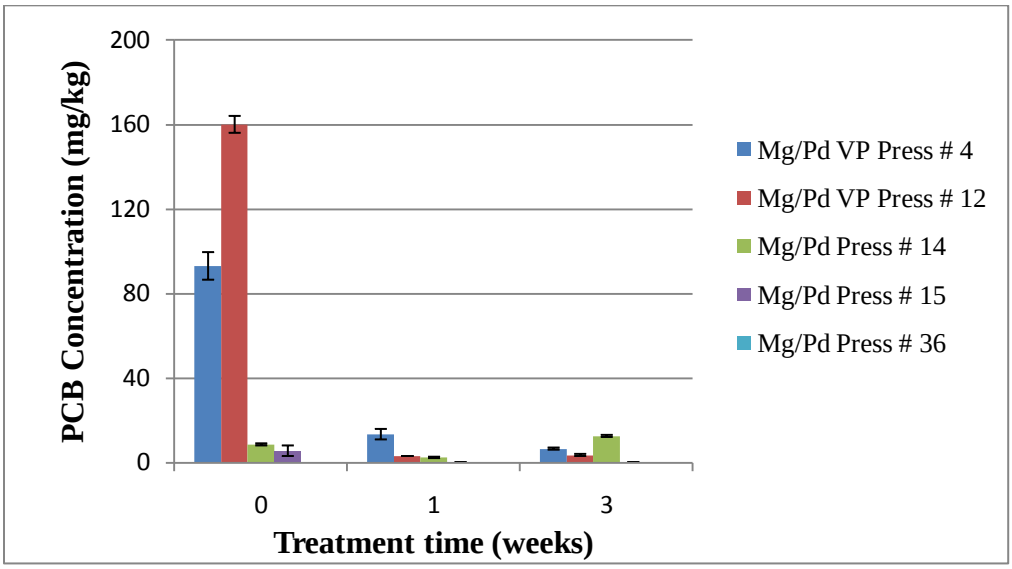


Figure 55: Staging area PCB in paint concentration over three weeks. Some samples were below detection limit.

Table 18 and Figure 55 show the PCB concentration in the BTS at the end of one and three weeks. At this time, all of the samples were below three ppm and no PCBs were detected in the BTS from press 15 or press 36.

Table 18: Staging area PCB concentrations in treatment paste over the treatment period of three weeks

Location Name	Treatment time (weeks)	Post average PCB conc. (mg/kg)
Mg/Pd VP Press # 4	1	2.2 ± 0.4
Mg/Pd VP Press # 4	3	1.5 ± 0.1
Mg/Pd VP Press # 12	1	0.3 ± 0.0
Mg/Pd VP Press # 12	3	0.4 ± 0.0
Mg/Pd Press # 14	1	0.5 ± 0.1
Mg/Pd Press # 14	3	0.2 ± 0.7
Mg/Pd Press # 15	1	BDL
Mg/Pd Press # 15	3	BDL
Mg/Pd Press # 36	1	BDL
Mg/Pd Press # 36	3	BDL

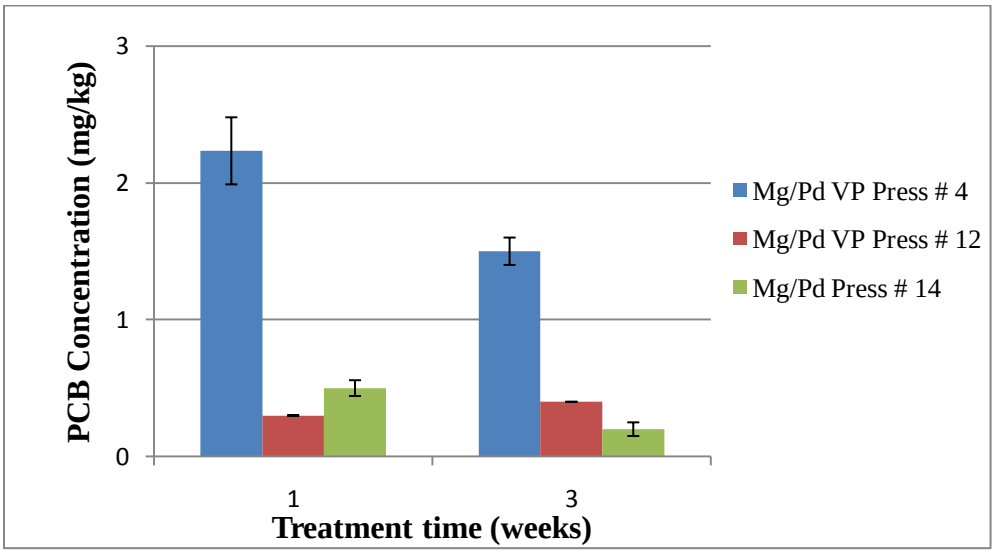


Figure 56: Staging area PCB in treatment paste concentration over three weeks. Treatment paste from Press #15 and Press# 36 were below detection limit

End of chapter remarks

The field study conducted at BAAP was an invaluable opportunity to demonstrate how BTS and NMTS can be used to remediate PCB-contaminated painted industrial parts. The technology was demonstrated to remove PCBs from painted metal as well as from painted concrete. The application of the treatment system and sealant to the vertical surfaces was relatively simplistic. Cracks in the sealant were easily fixed within the first week of treatment. Although there were a few setbacks concerning the treatment system's ability to adhere to a powdery surface, all treatment areas had sections that remained intact for the duration of the study. Post treatment paint was dramatically lower in Aroclor concentration with the largest portion of removal occurring within the first week. Many of the samples from the press houses and the staging area were remediated to concentrations under the EPA action limit of 50ppm. The exception to this was the nitrating house where multiple layers of paint and high concentrations kept many of the post-treatment concentrations in the thousands. In addition to lowering the PCB concentration in paint, the remediation method was also able to lower PCB concentrations at superficial depths of concrete beneth the paint. Large amounts of PCBs were detected in the NMTS after it was removed from the wall. Due to the varying thickness of the treatment system, a mass balance was not determined. NMTS and BTS, which were removed during the treatment process, were sent back to UCF for further degradation studies.

CHAPTER FIVE: OFF-SITE DEGRADATION

Once the contaminated treatment system was returned to the University of Central Florida, additional studies were planned to investigate the extent to which the PCBs could be further degraded. The following studies describe the laboratory experiments aimed at continuing degradation

Mg/C studies

Neat Mg/C degradation

The BTS contains Mg/Pd as the bimetal for PCB dechlorination. The milling process utilizes1% palladium on carbon graphite (Pd/C) as the source of palladium. Carbon has been observed as being very absorbent and it was unclear how this property would affect PCB degradation and analysis [51]. If the PCBs were absorbed onto the carbon they may became unavailable for degradation. They may also give a false low during PCB analysis if they are unable to be extracted completely. In addition, PCBs have been recorded to first adsorb onto the surface of the metal before dechlorination occurs and the amount that stayed on the surface without an acid wash had not been quantified [50]. The following experiment was conducted to determine the extent to which PCBs were absorbing onto the metal/carbon surface during degradation in acidified ethanol.

Magnesium was milled with carbon in the absence of palladium in the process described in Chapter 2 with the loading masses of 76.5g Mg and 8.5g C. The Mg/C with a mass of 0.5g was placed in each 20ml vial. A 4.95ml aliquot of absolute ethanol was added to the vial which was then spiked with 25µl of a 12,500 ng/µl solution of Aroclor 1254. A 50µl aliquot of glacial acetic acid was added and the contents of the vial were placed on a shaker table. At the extraction time, samples were extracted with 5.00ml of toluene as described in the extraction of neat metal studies section of Chapter 2. The initial PCB concentration of the solution was 14 µg/ml of Aroclor 1254.

It was expected that the absence of the catalyst, palladium, would inhibit any PCB degradation. Adsorption overtime would be apparent by the decrease in millivolt signal in the PCB envelope. The peak ratios, however, were expected to stay the same as seen previously in literature [50]. Figure 56 displays the chromatograms as a result of this study.

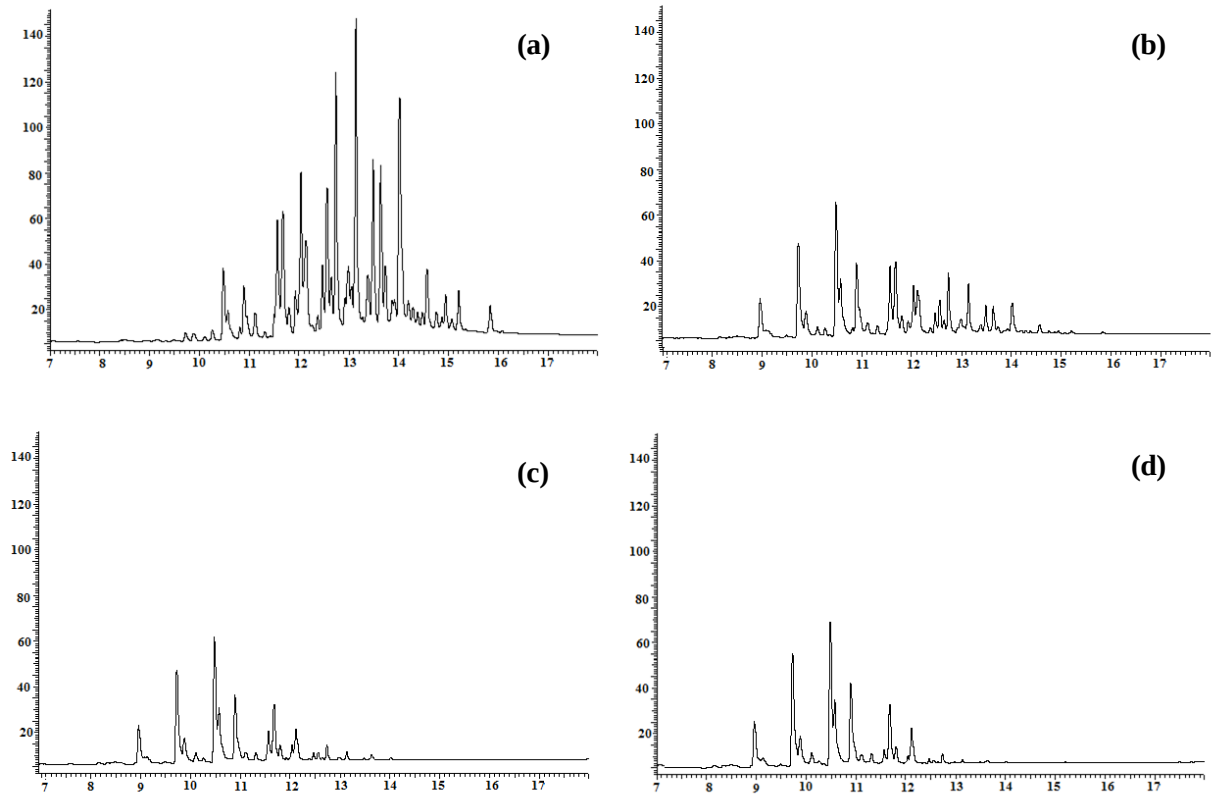


Figure 57: Aroclor 1254 after being exposed to Mg/C for a) 0hr b) 1 day c) 4 day d) 8 day

Within 24 hours there was a significant change in the PCB envelope indicating degradation. By the 8th day the majority of the peaks present in initial the Aroclor envelope were gone. There was a production of new peaks, specifically between the 9 and 10 min marks, as well as the disappearance of the later eluting peaks indicates that higher chlorinated PCBs were being dechlorinated to form lower chlorinated congeners. It became apparent that dehydrohalagination through the use of a bimetal was not the dechlorination process that was occurring.

Experiments in non acidified ethanol and in the absence of Mg/C

Once it was observed that dechlorination occurred in the absence of the palladium catalyst, additional studies were required to determine the role of the Mg/C and acetic acid in the dechlorination. The first study was designed to observe the effect that Mg/C had on PCB single congener 151 in the absence of acetic acid. Mg/C powder with a mass of 0.5g was measured into individual 20ml vials. An aliquot of 5.00ml of absolute ethanol was added to each vial and spiked with 20µl of a 1,250 ng/µl solution of PCB 151. To stop the reaction, 5.00ml of toluene was added and the solution was extracted as described in Chapter 2.

Samples were extracted at 0, 2, 4, 24, and 96 hours at which point no evidence of degradation occurred. Figure 57 shows the PCB 151 concentrations over initial concentrations (C/C^{o}) over 4 hours. In addition to the concentration remaining relatively consistent throughout the exposure time, no additional peaks were observed to have formed in the ECD chromatograms. It can be concluded that the acetic acid had a critical role in the degradation process of PCBs when exposed to Mg/C in ethanol.

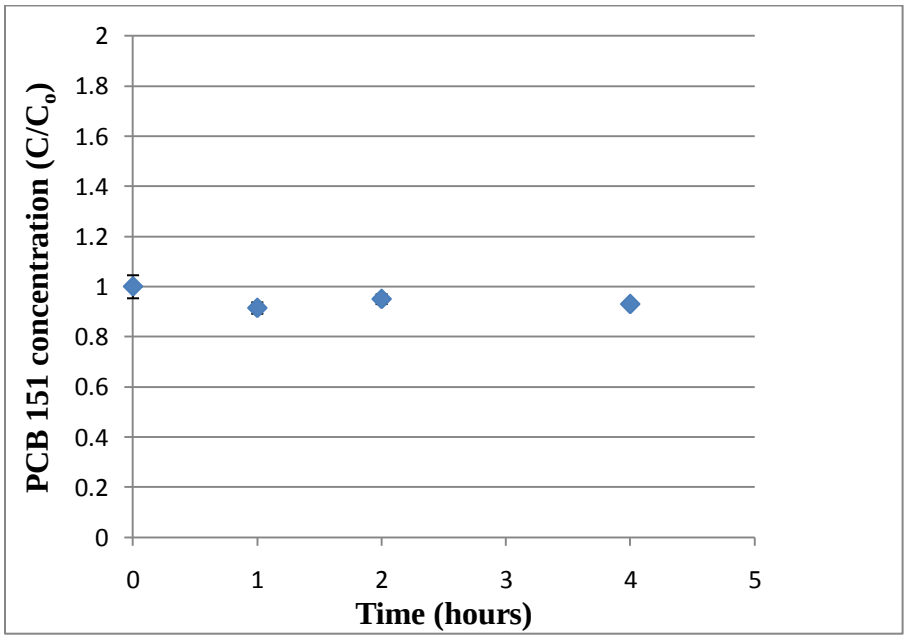


Figure 58: PCB congener 151 in non-acidified ethanol with Mg/C

A similar study was conducted to ensure that the acetic acid was not the only component required for dechlorination. For this second study, 4.95ml of absolute ethanol was spiked with 20µl of a 1,250 ng/µl solution of PCB 151 to which 50µl of glacial acetic acid was added. Even though no metal was added to the solution, the samples were extracted by the process described in the neat metal extraction section of Chapter 2.

Samples were extracted at 0, 1, 2, 24, and 96 hours and, as observed in the previous study, there was no evidence that degradation occurred. Figure 58 displays how the concentration of PCB 151 remained constant over 2 hours of being exposed to acidified ethanol. The samples were run in duplicate and the error bars are too small to be seen. The lack of degradation was expected since the stability of the PCB molecules makes it resistant to degradation by acids.

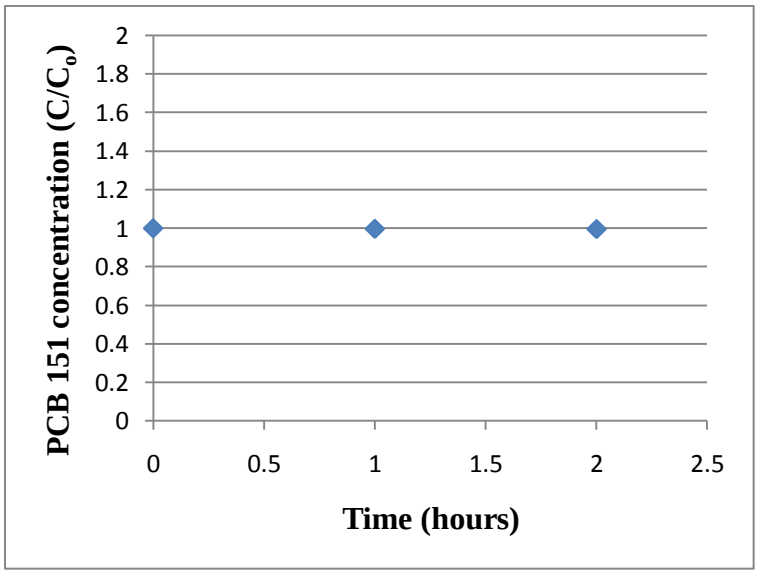


Figure 59: PCB congener 151 in acidified ethanol in the absence of ball milled Mg/C

Although simple in nature, the two studies described in this section prove that there is a unique process of degrading PCBs that had not been previously expressed in literature. The reaction is not happening through a bimetal reductive catalyst reaction as previously thought. The research team had conducted

years of research on bimetallic treatment systems in solvents involving water and methanol and it was expected that ethanol would act as a similar proton donor. In hindsight, this is why the initial ethanol studies did not degrade unless acetic acid was added. Since the palladium is not required for dechlorination yet acetic acid and metal are; studies on non-ball milled Mg powder were conducted.

Mg studies

The milling process was scaled up in order to produce enough bimetal for laboratory and field studies. Since each steel canister can mill 85g of bimetal and six canisters can be shaken at a time, 510g of bimetal can be produced approximately every 3 hours. Though this is significantly more than a traditional laboratory mill, cutting out the milling process entirely would remove additional time and cost from the remediation process. For that reason, studies were conducted to analyze the type of degradation that can occur with non-ball milled Mg powder

Mg in acidified ethanol

The first study utilizing Mg powder in acidified ethanol focused on the degradation of the single congener PCB 151. To do this, 0.25g of magnesium metal was added to 20ml vials containing 5.00ml of ethanol, 50.0µl of acetic acid and 25.0µl of 12,500ng/µl PCB 151 solution. After the designated time, 5.00 ml of toluene was added to stop the reaction and samples were extracted using the methods mentioned in Chapter 2.

Figure 59 shows the PCB 151 concentration (C/C_o) as a function of reaction time. The majority of the degradation occurred within the first 20min with the original congener being completely degraded within an hour.

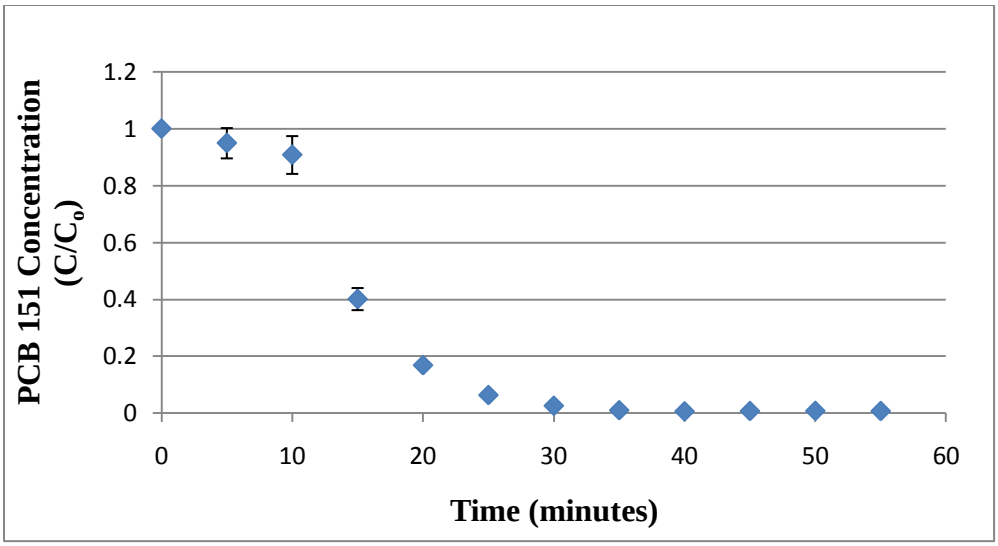


Figure 60: PCB congener 151 concentration over time after reacting with Mg in acidified ethanol

A similar study was then conducted on Aroclor 1254 to mimic the type of PCB mixture commonly found at contaminated industrial sites. Like before, 0.25g of magnesium metal was added to 20ml vials containing 5.00ml of ethanol and 50.0µl of acetic acid. The PCBs were added through a 25.0µl aliquot of a 1,250 ng/µl Aroclor 1254 solution. Samples were extracted every 20 minutes over a 220 minute time period through the process described in Chapter 2.

Figure 60 displays the Aroclor 1254 concentration (C/C_o) as a function of reaction time. The majority of degradation occurred within the first 100 minutes with more than 96% of the degradation occurring within 220 minutes.

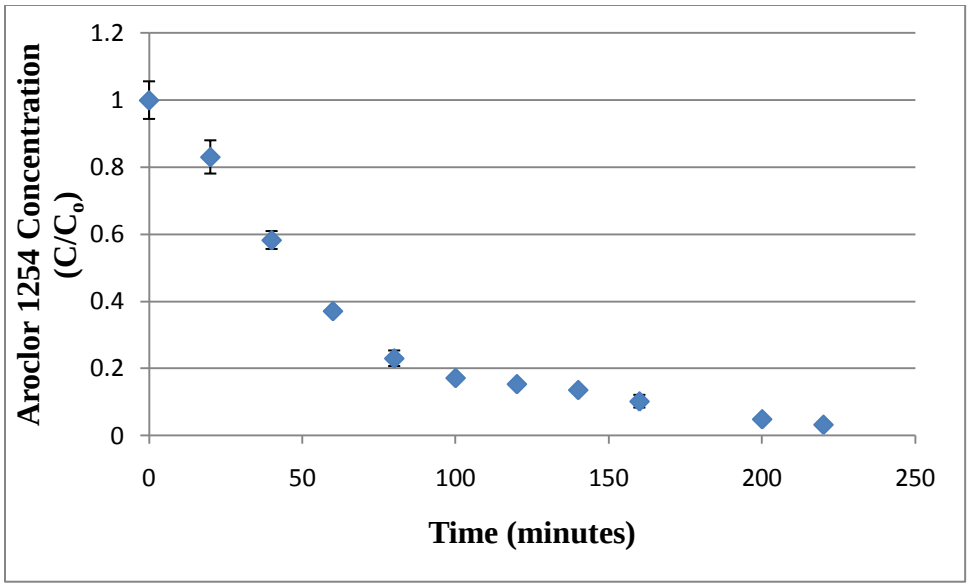


Figure 61: Aroclor 1254 concentration over time after reacting with Mg in acidified ethanol

Degrading a mixture of PCBs, like Aroclor 1254, requires multiple chlorines being removed from multiple congeners and it is understandable why it would take longer than degrading a single congener. Quantifying the degradation of single congeners, like PCB 151, is often used in laboratory studies due to the simplicity of analyzing one peak [52]. Analyzing mixtures of congeners becomes increasingly more difficult especially when attempting to quantify degradation. For example, the analysis of Aroclor 1254 described in figure 60 was based off of the peak areas of the 6 most prominent peaks in the mixture. As a result, the concentrations do not include total PCBs resulting from by-products.

Aroclor 1260 and 1254 degradation and byproducts

A few of the lower chlorinated PCB congeners, especially the ones that are monochlorinated, are not able to be detected on the ECD. In order to identify the byproducts of the degradation reaction when PCBs are exposed to zero-valent magnesium and acidified ethanol, extracted samples were analyzed on a Thermo GC-MS.

Aroclor 1260 and 1254 were degraded using the same process involving 10.00ml of a 100ppm solution of Aroclor mixture in ethanol added to vial containing 0.25g of Mg powder. Immediately, 0.100ml of glacial acetic acid was added to the vial and the samples were sealed and allowed to react. At predetermined time points, the samples were extracted with 10.00ml of toluene after which 4.00ml of solution were filtered through a Millex filter and continued with the extraction method as described in Chapter 2. The samples were analyzed by mass spectrometry with a method specifically suited to observe PCBs (as described in the MS methods in Chapter 2). Both Aroclor mixtures were extracted over 72 hours at which time both systems had finished observable degradation. Figure 62 shows GC/MS chromatograms from the degradation of Aroclor 1260. Similar to the ECD chromatograms, the more chlorinated congeners elute at later retention times. The y-axis displays relative abundance, as opposed to displaying a millivolt signal. The line drawn on top of the peaks classifies the PCB homologue for that type of compound. Figure 61 (a) shows that the original Aroclor 1260 contains a mixture of congeners containing four to eight chlorines. After an hour of degradation, congeners with two or three chlorines are evident while all of the congeners with eight and most of the congeners with seven are gone. Once the 24hr sample is extracted, the majority of the congeners contain four or less chlorines as seen in Figure 61 (d).

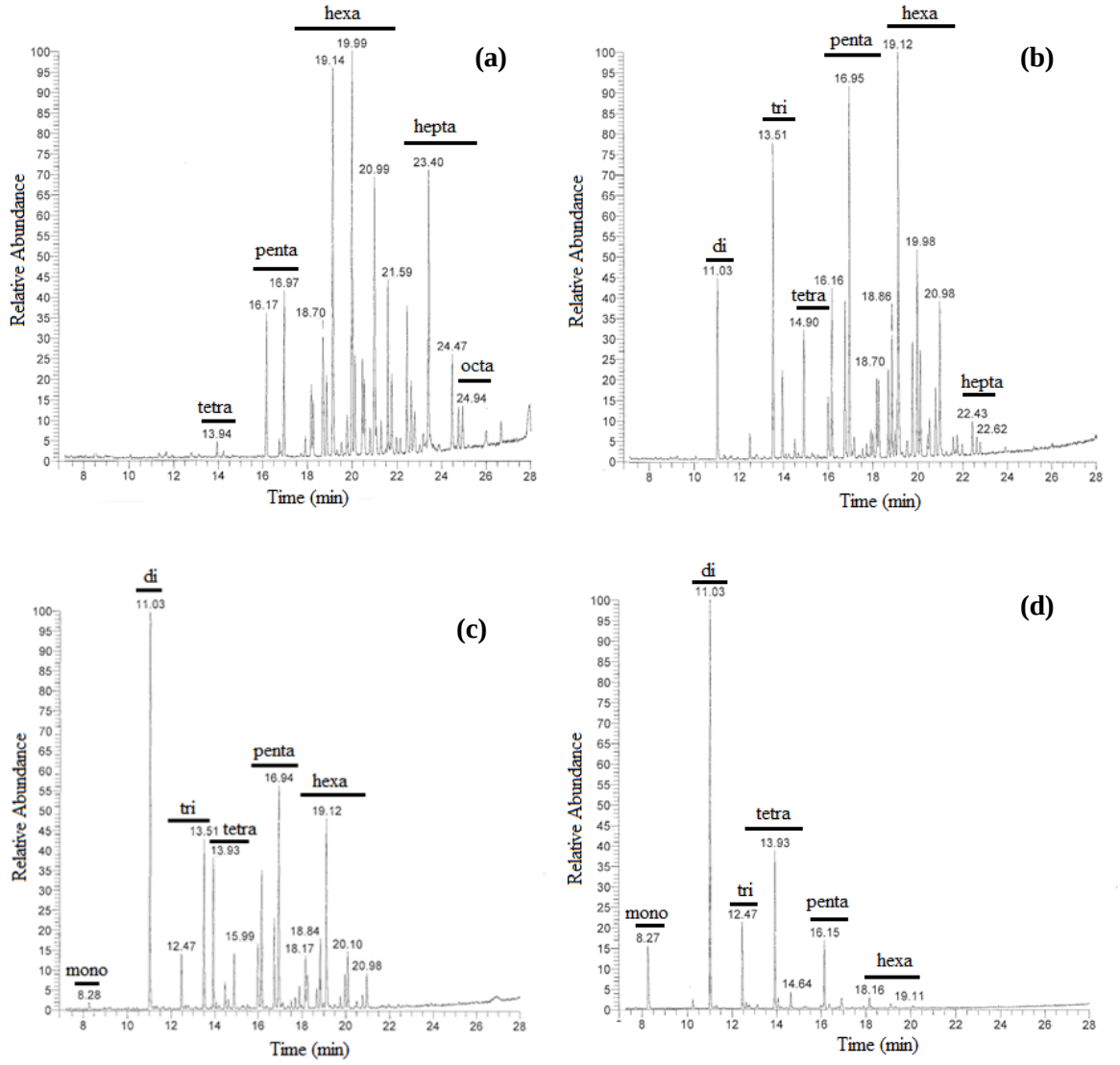


Figure 62: Mass spectrometry chromatograms for Aroclor 1260 reacting with Mg in acidified ethanol. a) 0hr b) 1hr c) 3hr d) 24hr

Samples were extracted at 48hr and 72hrs as well although no additional degradation could be observed. It appears that the PCBs that remain after 24 hours are mostly tetrachlorinated or less with a few pentachlorinated and hexachlorinated congeners.

The same procedure was used to observe the byproducts of Aroclor 1254 as seen in Figure 62. The mixture displayed in Figure 63 (a) contains congeners with four to seven chlorine substituents.

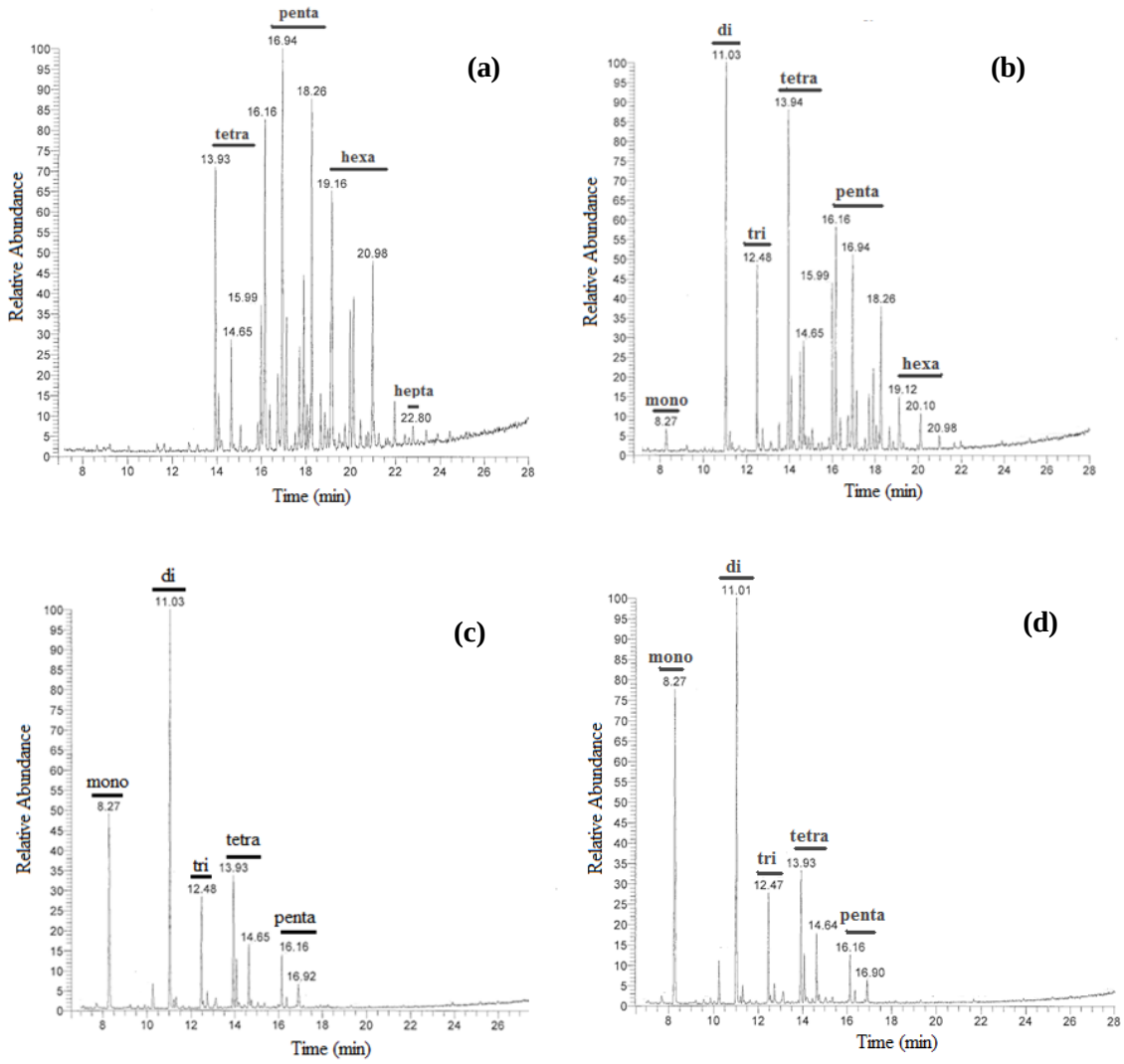


Figure 63: Mass spectrometry chromatograms for Aroclor 1254 reacting with Mg in acidified ethanol. a) 0hr b) 3hr c) 24hr d) 48hr

At the end of 48hrs, no congeners containing more than five chlorine atoms are detected and the majority of congeners contain only one or two chlorine atoms. The 72hr extract, though not shown, was analyzed and did not display further degradation compared to the 48hr sample.

Literature reports that a common byproduct of PCB degradation through reductive metals is biphenyl [33, 34]. In order to determine if biphenyl was a byproduct of PCB degradation in ethanol, the 48hr sample

from the degradation of Aroclor 1254 was run on the GCMS with a method designed to detect biphenyl. Figure 63 displays the chromatogram showing the detection of biphenyl at a retention time of 8.11min. This is an important point regarding PCB degradation because it shows that the system has the ability to dechlorinate a highly chlorinated Aroclor to biphenyl. The system containing Mg and acidified ethanol currently produces lower chlorinated congeners as the majority of the byproducts but the system may be adjusted to further degrade as the mechanism is better understood

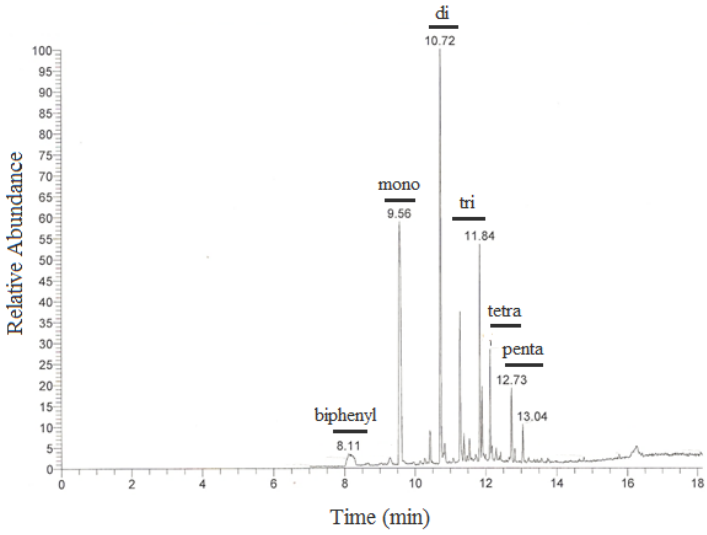


Figure 64: Mass Spectrometry chromatogram to show biphenyl production in Aroclor 1254 degradation

Degrading PCBs in activated metal treatment system

Once the zero-valent Mg was shown to degrade PCBs in acidified ethanol, a treatment system containing magnesium powder was developed. Magnesium coated in glycerol was added to NMTS along with acidified ethanol which activated the metal and enabled the system to degrade PCBs. As a result, this type of treatment system is generally referred to as an activated metal treatment system, AMTS. The following studies utilize AMTS to degrade Aroclor standards before moving on to degrade Aroclors from the BAAP in Wisconsin.

Mg spiked paste

Approximately 0.5g of NMTS was placed in 20ml vials and activated with 0.2g of a 50:50 mixture of Mg powder and glycerol as well as 250µl of acidified ethanol that was 10% acetic acid in volume. The mixture was spiked with 10µl of a 12,500 ng/µl solution of Aroclor 1260 in methanol and stirred with a glass pipette. The paste was extracted with 10.00ml of toluene as described in chapter 2. Figure 64 shows the Aroclor 1260 concentration (C/C^o) reducing over time with the majority of the peaks used for quantification degrading within 150 minutes.

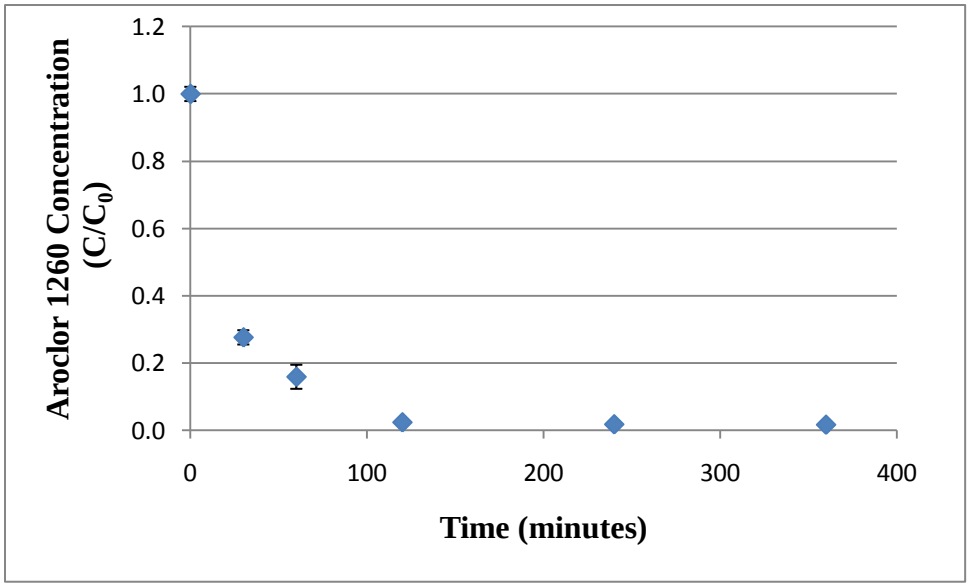


Figure 65: Aroclor 1260 degradation in AMTS

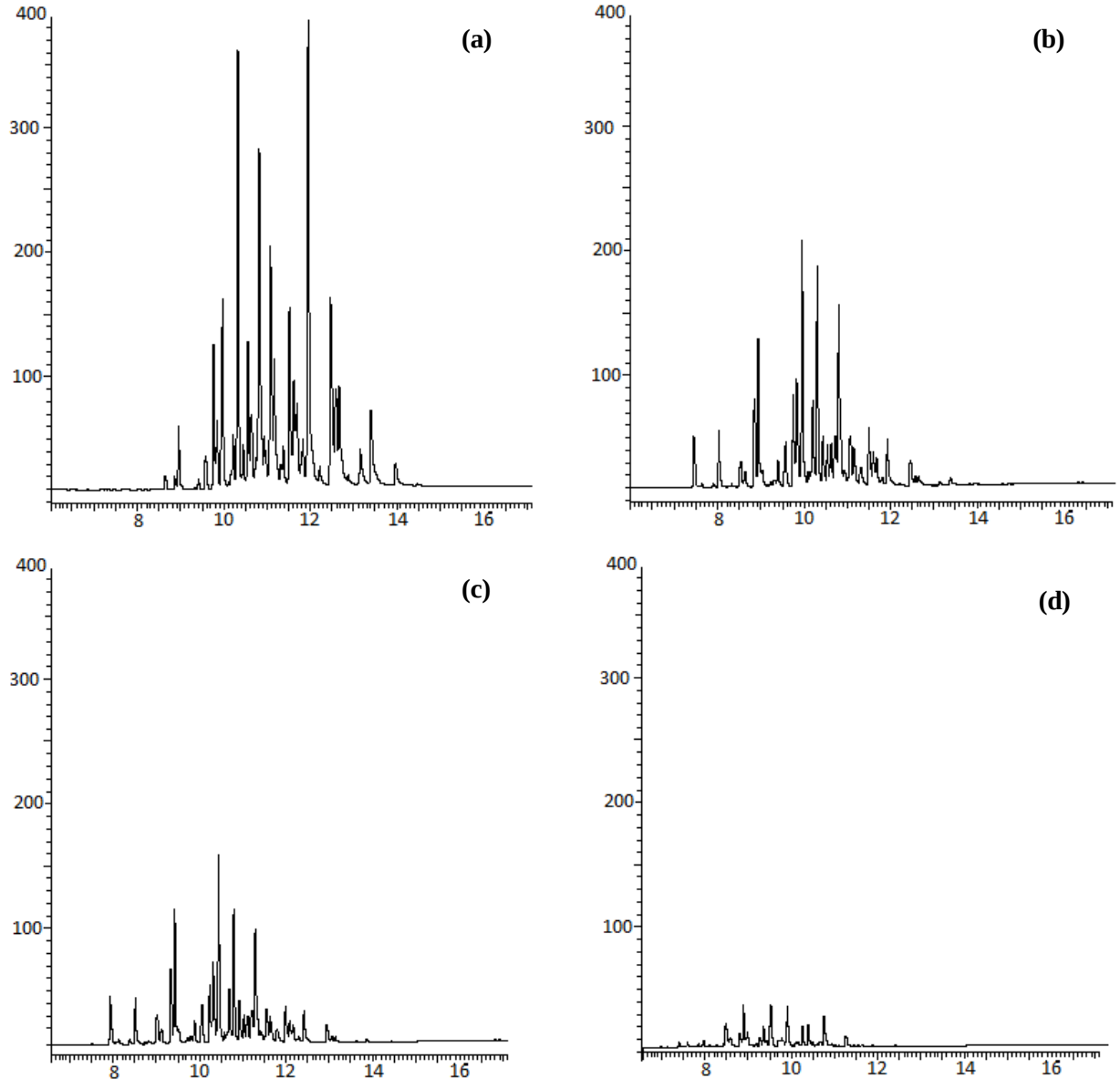


Figure 66: Chromatograms for Aroclor 1260 in treatment paste activated with Mg metal.

a) 0 hr b) 30 min c) 60 min d) 120 min

Figure 65 shows the corresponding chromatograms of Aroclor 1260 as it was degraded in the AMTS. The starting concentration of the treatment system was 167ppm. The final concentration was less than 9ppm. Once the ability of the AMTS to degrade an Aroclor standard was established, the next objective was to treat the contaminated treatment systems from the field demonstration.

Remediating contaminated paste

The NMTS that was returned to the UCF laboratory after being used in the BAAP field study contained a wide range of PCB concentrations, most of which were above the EPA action limit of 50ppm. Press houses 6810-11 and 6810-36 both had moderately high concentrations in the hundreds of ppm, while the nitrating house 6657-02 had very high concentrations in the thousands of ppm. This study observed the ability to degrade PCBs already in the inert matrix of the NMTS by the addition of metal and acidified ethanol. Both Mg/Pd and Mg powder were used in the initial experiment.

Approximately 0.5g of contaminated paste was placed in a 20ml sample vial and combined with 0.2g of a 50:50 mixture of glycerol and metal (Mg or Mg/Pd). The treatment system was activated by the addition of 1.00ml of acidified ethanol that was 10% acetic acid by volume. The samples were extracted using 10.00ml of toluene as described in chapter 2. All of the samples were performed in duplicate except for the day three samples with Mg whose duplicates were unintentionally compromised.

Table 19: Remediating contaminated NMTS through addition of acidified ethanol and Mg/Pd or Mg powder

	PCB concentrations (mg/kg)				
		Mg		Mg/Pd	
Sample	initial	3 day	7 day	3 day	7 day
NM 6810-36 1 wk	56.0 ± 4.24	16.0	16.9 ± 8.79	14.0 ±1.50	36.0± 16.0
NM 6810-36 2 wk	95.3 ± 18.1	2.41	3.21 ± 0.450	3.84 ± 0.329	3.54 ± 0.138
NM 6810-11 3 wk	162 ± 60.1	48.3	53.3 ± 7.15	39.7 ± 4.57	18.3 ± 5.53
NM 6657-02 1 wk	298 ± 60.1	22.0	29.3 ± 8.89	96.6 ± 14.0	106 ± 13.0
NM 6657-02 2 wk	1554 ± 206	31.8	29.6 ± 8.90	128 ± 1.00	171 ± 24.0

Table 19 displays the results of the study at three days and seven days for both Mg and Mg/Pd. The treatment system with the added Mg powder was able to degrade all but one of the samples to below the action limit. It was particularly effective at degrading the PCBs in the NMTS from the nitrating house 6657-02. The treatment system with the Mg/Pd also degraded the PCBs much below their initial concentrations.

PCB contaminated NMTS was not the only type of treatment system that returned from the BAAP site. BTS was also acquired from all of the locations and often contained PCB concentrations higher than the 50ppm action limit. Initially, 2.00ml of acidified ethanol that was 10% acetic acid by volume was added to the contaminated BTS in hopes that the added acid would reactivate the metal. This was done on BTS from three different locations and sampled in duplicate over a three day and seven day period, at which time no degradation had occurred. It was then decided to treat the BTS like the NMTS was previously degraded by adding additional metal and acid.

The following study was intended to degrade PCBs from BTS as well as NMTS over a 21 day period. Zero-valent magnesium was chosen for this experiment due to its ability to degrade PCBs as seen previously in the study, as well as its economic prospective compared to Mg/Pd. The 21 day time period was intended to see how long the system would continue to degrade PCBs

Similar to previous studies, 0.5g of contaminated treatment system (NMTS or BTS) were placed into 20ml sample vials. This time, however, twice the amounts of reagents were added. Therefore, 0.4g of the 50:50 metal glycerol mixture (m/m) was added as well as4.00ml of acidified ethanol. The samples were still extracted in 10.00ml of toluene as described in Chapter 2.

Table 20: Remediating contaminated BTS and NMTS through addition of Mg powder and acidified ethanol

	PCB concentration (mg/kg)			
Sample	Initial	7 day	14 day	21 day
6657-02 NM Vp wk 3	1781 ±386	2.04	3.63 ± 0.450	2.06 ± 0.010
6657-02 Mg/Pd Sil wk 3	716 ± 104	219 ± 36.9	160 ± 47.8	185 ± 14.4
6657-02 Mg/Pd Vp wk 2	464 ± 68.7	122	120 ± 24.0	83.0 ± 13.0
6810-36 NM Vp wk 3	152 ± 7.78	1.01	1.50 ± 0.71	1.00 ± 0.00
6810-36 Mg/Pd Vp wk 3	34.3 ± 17.0	20.0 ± 8.76	27.4 ± 11.7	15.5 ± 0.69
6810-11 NM Vp wk 3	162 ± 60.1	4.17 ± 2.30	2.10 ± 1.09	1.75 ± 1.07

Added Mg powder and acidified ethanol degraded PCBs in both contaminated NMTS and BTS as seen in Table 20. All of the NMTS were able to degrade past the 50ppm limit. The samples of BTS, though significantly lower than the initial concentrations, repeatedly degraded less than the samples of NMTS.

This implies that the Mg/Pd present in the contaminated paste may inhibit the further degradation with added reactants.

Dip test

A treatment bath method intended to remediate PCBs from painted metal parts was previously introduced in Chapter 3. The initial study observed the ability of the NMTS to remove PCBs from an irregularly shaped painted piece of metal. At the end of the field demonstration, additional samples were sent to UCF from the BAAP in Wisconsin and were remediated with this method. Since the AMTS was now established, the newly obtained metal parts were dipped in a treatment bath containing zero-valent magnesium and acidified ethanol. An activated treatment bath was created by combining 6.2kg of the NMTS with 5.56L of acidified ethanol that was 1% acetic acid (v/v). This was then activated with 650g of magnesium coated with 650g of glycerol. The metal parts were immediately submerged into the treatment system and were sealed after 5 hours and left to react. After one week, the metal pieces were removed and sampled to determine PCB concentration. Approximately 0.05g of paint from the metal parts were analytically massed into 20ml vials and extracted with 10.0ml of toluene. The AMTS was sampled by removing approximately 0.8g of paste from the metal part after it was removed from the bath. Samples were analyzed in triplicate. Figure 67 is a photograph of metal piece C after the one week sampling. As seen in the photo, the metal itself, copper in color, is exposed in areas where the light green paint has been removed. The gray area is where the AMTS is still fixed on the surface.

Figure 67: Dipped piece of metal, piece C, after treatment

Table 21: Concentrations for dipped piece of metal

	PCB concentration (mg/kg)		
Sample	Pre (paint)	Post (paint)	Post (paste)
Piece A	70.93 ± 4.69	3.81 ± 0.12	BDL
Piece B	65.61 ± 5.79	1.23 ± 0.62	BDL
Piece C	26.65 ± 11.93	BDL	BDL

Table 21 displays the PCB concentrations for the paint and the treatment paste after one week. The metal pieces used in the activated treatment bath were much lower than the painted piece of metal described in Chapter 3. The PCB concentration of the paint was well below the action limit and in one section was not able to be detected. The treatment paste was sampled as close to the metal piece itself in hopes of quantifying degradation. Due to the inability to detect PCBs it is unclear if the PCBs simply migrated into the treatment system and dispersed or if they were actually degraded. Studies described previously in the chapter, however, imply that PCB degradation occurred.

End of chapter remarks

In efforts to continue the remediation process once the field samples were returned to UCF, a novel degradation system was discovered using zero valent magnesium and ethanol acidified with acetic acid. The use of zero valent metal, compared to the previously used bimetal, could potentially save treatment costs in future remediation projects. In vial studies, the magnesium and acidified ethanol system is able to degrade single congener 151 within 60 minutes and the majority of Aroclor 1254 in 220 minutes. The byproducts of this reaction include lower chlorinated PCBs and biphenyl. The system was incorporated into the NMTS to create an AMTS in which PCB degradation occurred. Magnesium powder and ethanol acidified with acetic acid were added to the contaminated NMTS and BTS from the recent field demonstration to continue the remediation process. The initial data indicates that activating contaminated NMTS was more effective at degrading PCBs than activated BTS. In the future, a two step method may be derived from the idea of removing PCBS from a painted structure with NMTS first before activating with metal and acidified ethanol in an onsite container. Similarly, an activated treatment bath demonstrated an alternate treatment method for painted metal parts.

CHAPTER SIX: SMALL SCALE FIELD TEST AND EXTENDED STUDIES

The success of the AMTS opened up the possibility of remediation without the added cost of palladium or the added labor of milling. The first field study at BAAP, displayed the ability of the AMTS to degrade previously contaminated treatment paste removed from industrial painted surfaces. An opportunity to remediate paint samples from a second site allowed the AMTS to be tested in both the removal and degradation of PCBs in paint.

Background of Site and types of samples

The second field site was an old manufacturing facility in the state of New York. The site contained various types of PCB-contaminated materials including paint, concrete, caulking, oil, sludge, and soil. The studies in this chapter, however, solely describe the remediation of the PCB contaminated paint. Paint chips from 8 different locations were sent to UCF to be treated with AMTS including samples from structural components of the building as well as machine parts. In the laboratory, the paint chips were treated with AMTS and were monitored over a three week period.

Experimental setup

Approximately 0.15g of paint chips were analytically measured in individual vials. AMTS was added to the paint chips in 0.8g aliquots and the contents were mixed with a glass pipette. The glass pipette was broken and left in the vial to ensure all contents remained. After the designated treatment time, 10.00ml of toluene was added to the mixture and the PCBS were extracted and analyzed as described in Chapter 2. Note that the paint chips and the AMTS were not separated and were therefore extracted and analyzed as one sample.

Data and results

Table 23 reports the PCB concentrations in each sample over three weeks. The first four samples on the table: G21, E23, D21, and Lathe were done in an initial experiment to gauge the treatment timeframe.

Since there was a large amount of degradation still occurring between the seventh day and third week, as seen in Figure 67, the second study, containing Blanchard, C15 column, C7 truss, and C15 truss were only sampled on week three. This is displayed in Figure 68. It can be seen that the AMTS was able to extract and degrade up to 98% of the PCBs that were originally in the contaminated paint. Even samples in the thousands of ppm were able to be degraded around or below the 50ppm limit.

Table 22: PCB concentrations over time

	Initial concentration (mg/kg)	7 day concentration (mg/kg)	3 week concentration (mg/kg)
G21	1390 ± 152	392 ± 31.0	42.6 ± 23.5
E23	831 ± 42.0	433 ± 136	51.2 ± 15.5
D21	2290 ± 132	491 ± 155	104 ± 21.0
Lathe	2397 ± 16.2	1050	52.3 ± 5.77
Blanchard	2780 ± 88.5		55.7 ± 9.01
C15 column	4540 ± 181		385 ± 43.0
C7 truss	1000 ± 42.0		21.6 ± 0.30
C15 truss	1380 ± 79.0		42.0 ± 28.8

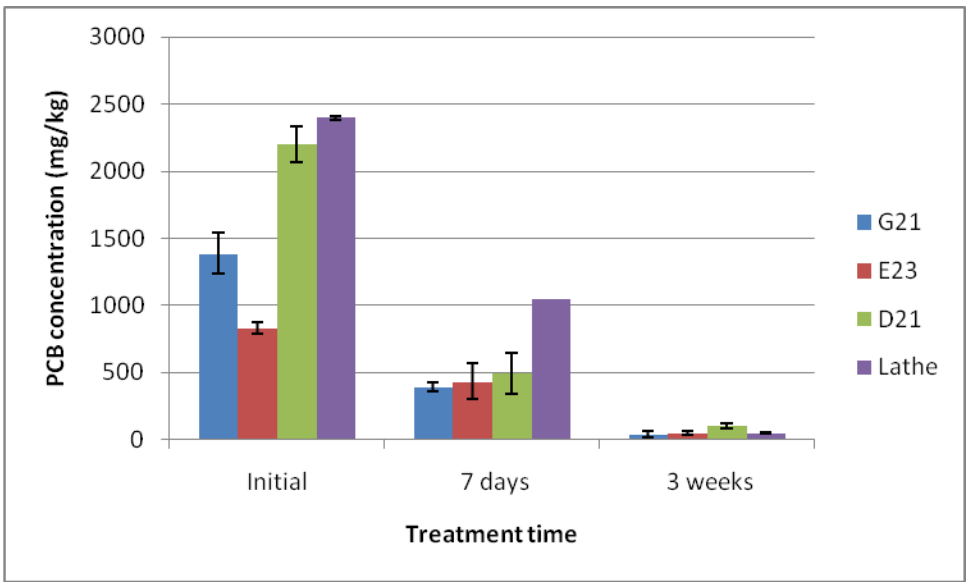


Figure 68: PCB concentrations over three weeks

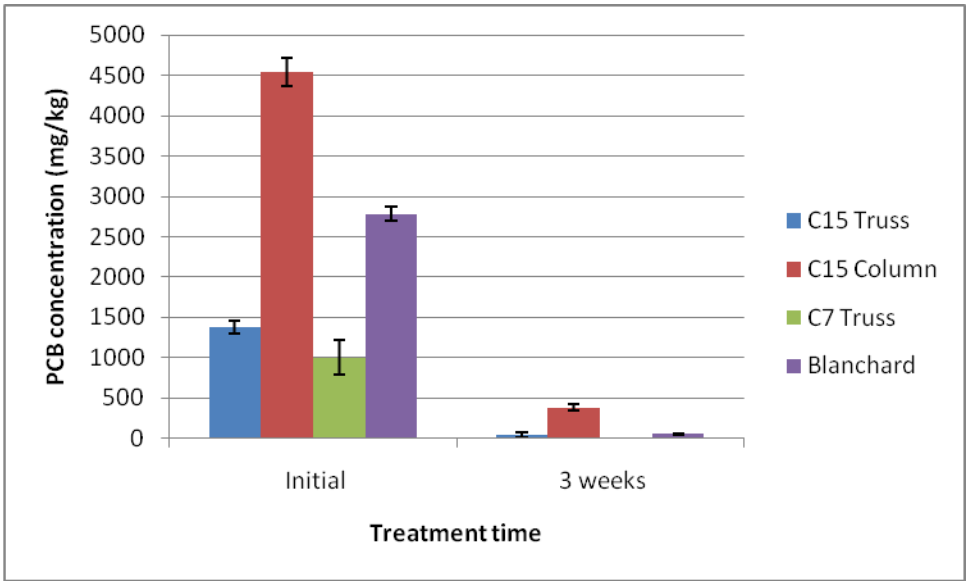


Figure 69: PCB concentrations over three weeks

Degrading PCBs from contaminated paint chips is an important step in working towards the scaled-up use of AMTS. The system has to be able to pull the PCBs out of the paint before they can be degraded which in this case, that was accomplished. In regard to the submerged paint chips, AMTS was able to fully surround large surface areas of the paint, compared to a scenario where the paint was still affixed to a metal or concrete surface. Being sealed in a sample vial also limited solvent evaporation. Whether or not these results could be mimicked on a vertical surface using the 'apply and seal' method has not been determined. However, the utilization of Mg in acidified ethanol as a novel degradation system has promise for large scale environmental remediation.

Extended studies

A better understanding of the mechanistic details will allow the treatment system to be modified for optimal degradation. Although beyond the scope of this dissertation, additional studies will have to be performed in order to enhance PCB degradation via this technology. The following sections contain

observations that may prompt future studies which will lead to an understanding of the chemical processes occurring.

PCB Removal vs. Reaction Kinetics

The time it takes to remove the PCBs from a painted surface may or may not align with the degradation kinetics. For paint that is particularly difficult to penetrate, as well as remediation in less than ideal conditions, the degradation kinetics of the treatment system may slow down before the PCBs are even removed from the paint. Therefore additional studies should be done to determine how long the paste can stay active before introducing PCBs. Once this is understood, field samples could be tested to establish a PCB removal time period. With this information, personnel could decide whether it is better to apply the AMTS to the surface for a one step degradation method, or if the NMTS should first remove the PCBs and then be placed in a container and activated with metal to degrade the PCBs in a second step.

Added acid and/or metal to enhance degradation

One of the first steps aimed at continuing degradation in the treatment system once it apparently ceased was to simply add more reactants. NMTS was prepared as described in Chapter 2. In each 20ml vial, 0.45g of NMTS was combined with 0.2g of a 50:50 mixture (m/m) of glycerol to Mg powder. A 0.300ml aliquot of 10% acetic acid in ethanol (v/v) was added followed by 10µl of a 12,500ng/µl Aroclor 1254 solution in toluene. The reaction sat for 3, 7 and 14 days at which time samples were extracted with 10.00ml of toluene and analyzed for PCBs. The samples were run in duplicate and were analyzed on the 15th day at which time it was observed that no further degradation had occurred after three days. Fortunately, there were four remaining samples, two had been intended to be extracted on the 21st day and the last two had been intended to be extracted on the 28th day. In an effort to push the reaction further, these four samples were used as part of a second study. Two of the vials received additional acid in the form of 0.25ml of 10% acetic acid in ethanol (v/v). The second two vials received additional acid and additional metal. The acid was added like the previous samples with the addition of 0.25ml of 10% acetic acid in ethanol (v/v) as well as 0.20g of the 50:50 mixture (m/m) of glycerol to Mg powder. The

samples were allowed to react for another three days before being extracted with 10.00ml of toluene and analyzed for PCBs.

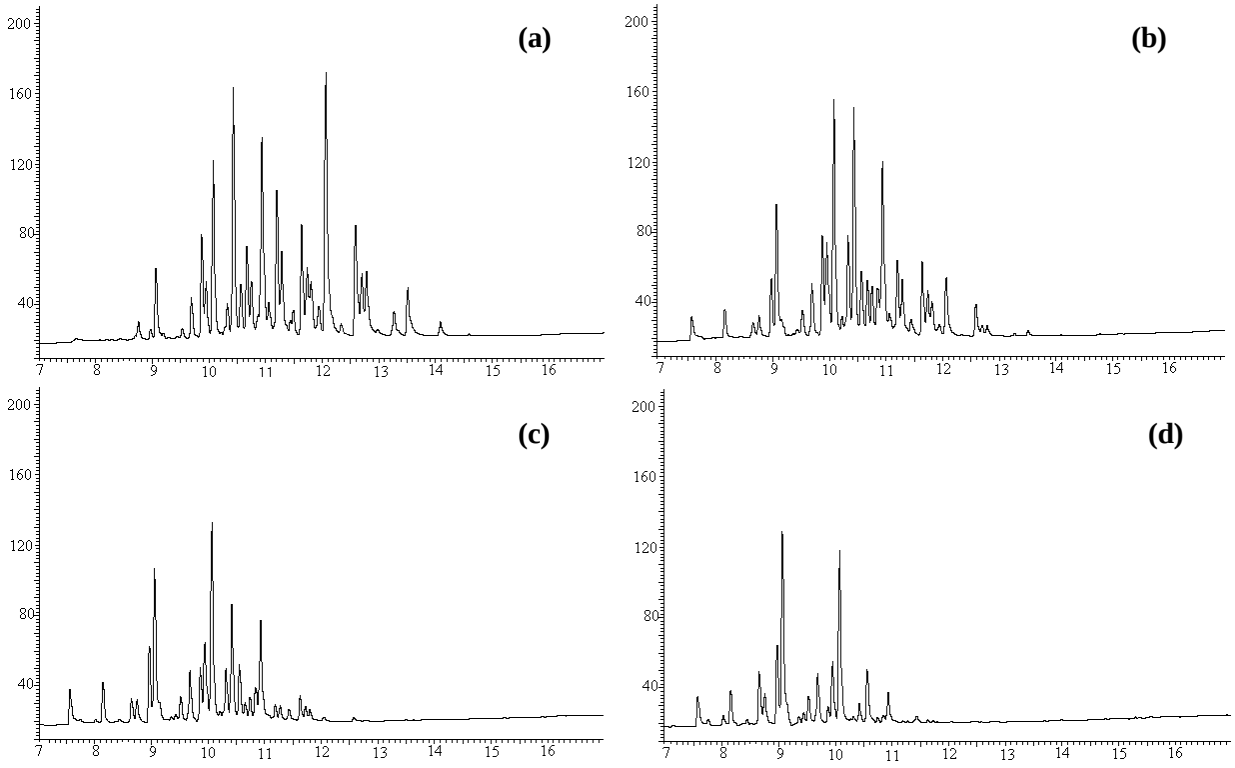


Figure 70: Chromatograms of Aroclor 1260 after reacting with Mg in acidified ethanol a) 0hr b) 3day once reaction had stopped c) after adding metal and acid d) after adding only acid

Figure 69 shows chromatograms for the second part of the study. The first chromatogram is an image of the 1260 before reacting with the AMTS. The second chromatogram is from the sample for the third day. The seventh and fourteenth days, not shown in figure 69, reported the same peak ratios indicating that degradation had ceased. Chromatograms c and d display the envelope after the PCBs reacted another three days with either additional acid with metal or additional acid only. The disappearance of the later peaks, particularly after 10 minutes, as well as the larger peak at 9 minutes in chromatogram d implies that more degradation occurred when just additional acid was added. The duplicate chromatograms agree with this implication as well. These findings could lead to additional studies intended to reactivate the

system once degradation has occurred. It will need to be determined if acid can be added every three days until all of the PCBs have been degraded or if there is some endpoint at an incomplete degradation that cannot be passed. In a treatment bath method, acid could be easily added to the system and agitated to distribute. It may even be possible to inject the AMTS already applied to a vertical surface with additional acidified solvent and patch up the sealant if needed.

Order of addition

The two ways that PCB degradation has been described in this paper include PCBs that are introduced into an active treatment system or PCBs that are degraded after they have been contained in the treatment system. In essence, there are two main orders in which PCBs have been added to the degradation system. Initial studies have shown that the order of addition may impact the extent to which the compound will degrade.

To show this, two types of methods were used to introduce PCBs. During the first trial, 10µl of 12,500 ng/µl of PCB 151 was added to 0.5g NMTS immediately followed by 250µl of 10% acidified ethanol and 0.2g of a 50:50 mixture of magnesium powder and glycerol. The second trial started with the 250µl of 10% acidified ethanol and 0.2g of a 50:50 mixture of magnesium powder and glycerol added to the 0.5g NMTS before finally adding 10µl of 12,500 ng/µl of PCB 151. Figure 70 displays the chromatograms of the results. The peak ratios for the system where the PCBs were added last show more degradation.

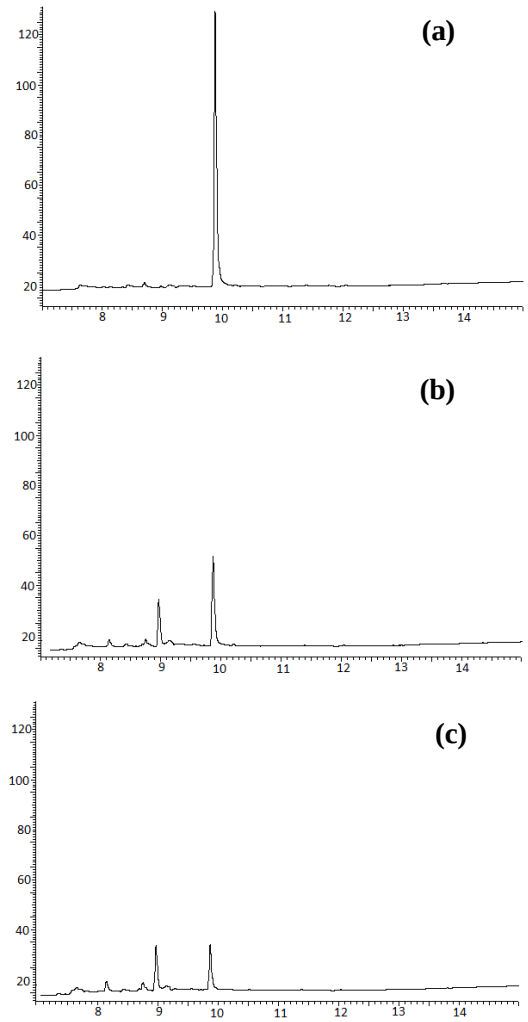


Figure 71: PCB-151 Chromatogram

a) 0hr b) PCBs added before acid and Mg c) PCBs added after acid and Mg

Although the study is simply an initial observation, especially since the reaction was not done in duplicate, it was conducted because previous vial studies appeared to favor certain orders of addition of reactants. Whether or not it is better to remove the PCBs from the paint before activating the treatment system is yet to be determined.

The role of acid and reaction pH

The incorporation of acid in the ethanol solvent established a novel degradation system with magnesium in the absence of a metal catalyst provided by a bimetal. It is expected that the acid is the source of the hydrogen and is therefore critical in the degradation process. Initial laboratory studies indicate that in addition to the type of solvent used, degradation is dependent on the type and amount of acid used. The solvent system observed during vial studies with Mg powder is neutral as indicated by universal litmus paper. As the reaction progresses however, the solution becomes increasingly basic. It is unclear if this is what stops the reaction from progressing. Studies examining the impact of a buffered solution could be of value as well as exploring other realms of hydrogen donation. Either way, the role of acid and its effect on reaction pH may be the key to better understanding the degradation process.

CHAPTER SEVEN: CONCLUSIONS

Since their ban in the late 1970s, polychlorinated biphenyls have been studied in regard to their impact on human health and the environment. PCBs have been associated with an extensive variety of negative health effects and have been classified as a probable human carcinogen by the EPA. PCBs are more common in industrial areas but can also be found in remote locations due to their ability to travel long distances. Capacitors, transformers, hydraulic fluid, oils and paint contaminated with PCBs are examples of point sources that can lead to environmental exposure. Once in the environment, PCBs can pose a long term threat due to the stability of the biphenyl structure, which makes PCBs resistant to degradation. Large structures painted with PCB-contaminated paint are particularly difficult to address since the size of the material makes incineration and disposing in hazardous landfills expensive. The objective of this dissertation was to develop a treatment system that could be used to remediate contaminated painted surfaces. The work was inspired by the degradation abilities of reductive metals, which, as literature has shown, have the prospects to develop in to an in-situ remediation technology.

The bimetal, Mg/Pd, which was produced by mechanically alloying Mg powder with Pd/C was incorporated into an application media which together made up the bimetallic treatment system, BTS. The BTS was designed to adhere to a vertical surface, remove PCBs from the paint and then degrade them into inert byproducts. The solvent is important for the removal and degradation processes, thus steps were taken to maintain the maximum solvent retention. The BTS should be applied to an approximate thickness of 12.7mm and then be sealed with five coats of vinyl sealant. On a large scale, the application and sealing process should occur as quickly as possible although laboratory studies have shown that the treatment system can still remove more than 90% of the PCBs in three days even after 36% of the solvent is lost before being sealed. Site-specific conditions were taken into consideration including the porous nature of the painted concrete and the cold temperatures expected at the time of the field demonstration. Laboratory studies determined that PCBs were not being pushed further into the

concrete during the removal period. In addition, temperatures as low as -19^{o}C did not appear to have as big of an impact on the removal ability as did the number of layers and type of paint. A dip method was established for contaminated machine parts that would be difficult to seal with the vinyl sealant due to their irregular shape. The immersion process removed 97-99% of PCBs in the paint where the initial concentrations were as high as 48,000mg/kg.

The laboratory studies worked toward the eventual field application where four sites at a DOD facility were treated with BTS and a non-metal treatment system, NMTS, over a three week period. Two types of sealants were used including a vinyl sealant and a silicon sealant. The paint at two of the sites was very powdery and made it difficult for the treatment system to stay affixed to the surface. The treatment system at the other two sites remained intact throughout the entire treatment process. All of the locations, with the exception of the staging area, were sampled once a week and analysis was done at the University of Central Florida. The majority of PCB removal occurred within the first week of application of the treatment system. Several of the samples from the press houses and the staging area show that PCB levels were reduced to below the EPA action limit of 50 mg/kg. The nitrating house had particularly high concentrations of PCBs, some of which reached 40,000mg/kg. Lower percent removal of PCBs at this site may have been a result of these high concentrations as well as the presence of numerous layers of paint. Another reason may be that the paint was resistant to softening since samples from this location were not available for testing in the pre field-application part of the project.

Additional studies performed in the laboratory post field study indicated that in ethanol acidified with acetic acid, it is not necessary to include Pd in the reductive metal system. Aroclor 1254 was observed to degrade more than 96% within the first 220minutes of reacting with magnesium in ethanol that was 1% acetic acid (v/v). The reaction system was able to degrade PCBs all the way to biphenyl with the most abundant byproduct being lower chlorinated biphenyls like monochlorinated biphenyl and dichloronated biphenyl. Mg powder was included into the previously developed treatment system to make an activated metal treatment system, AMTS. The AMTS was shown to degrade PCB standards as well as PCBs

already incorporated into contaminated treatment paste. When Mg metal and acidified ethanol were added to contaminated treatment paste, both BTS and NMTS, more degradation occurred when metal was not already present in the system. Therefore, if degradation is desired after the PCBs go into the treatment system paste, the NMTS would give best results.

The degradation ability of the AMTS was evaluated with paint chips from a manufacturing facility in New York state. The initial concentrations of the paint chips ranged from 831-4,500mg/kg. Over three weeks, vial studies containing AMTS were able to lower the PCB concentrations of the paint to near or below the 50mg/kg action limit.

The use of zero valent magnesium in the presence of ethanol and acetic acid has been proven to be a promising method to remediate PCB-contaminated painted structures. Additional studies will need to be done to determine the exact mechanism of degradation. Reaction kinetics need to be understood in order to align with the period of PCB removal from the painted structure. The role that the acid and the pH play in the mechanism could eventually determine how the treatment system is enhanced and the extent to which it can degrade PCBs. For painted structures where PCBs are particularly difficult to remove, additional applications of the treatment system may be an option.

The work presented in this dissertation has made a significant contribution to the options available for PCB-contaminated painted structures. There are no other methods that are able to remove and degrade PCBs without compromising the structure. Although both of the field sites described are no longer in use, this technology could be appealing to those wishing to remove PCBs from buildings that are still needed. Schools and buildings of historical relevance, for example, could be treated to meet EPA regulation and repainted for future use.

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REFERENCES

1. Erickson, M.D., *Analytical Chemistry of PCBs* 2nd ed. 1997, Boca Raton: CRC press inc.

2. Borja, J., et al., *Polychlorinated biphenyls and their biodegradation.* Process Biochemistry, 2005. **40**(6): p. 1999-2013.

3. Wiegel, J. and Q. Wu, *Microbial reductive dehalogenation of polychlorinated biphenyls.* FEMS Microbiology Ecology, 2000. **32**(1): p. 1-15.

4. Andersson, M., R.T. Ottesen, and T. Volden, *Building materials as a source of PCB pollution in Bergen, Norway.* Sci. Total Environ., 2004. **325**(1-3): p. 139-144.

5. Field, J.A. and R. Sierra-Alvarez, *Microbial degradation of chlorinated dioxins.* Chemosphere, 2008. **71**(6): p. 1005-1018.

6. Van Gerven, T., D. Geysen, and C. Vandecasteele, *Estimation of the contribution of a municipal waste incinerator to the overall emission and human intake of PCBs in Wilrijk, Flanders.* Chemosphere, 2004. **54**(9): p. 1303-1308.

7. Kuusisto, S., et al., *PCB-contaminated dust on indoor surfaces - Health risks and acceptable surface concentrations in residential and occupational settings.* Chemosphere, 2007. **67**(6): p. 1194-1201.

8. Harrad, S., et al., *Polychlorinated biphenyls in domestic dust from Canada, New Zealand, United Kingdom and United States: Implications for human exposure.* Chemosphere, 2009. **76**(2): p. 232-238.

9. *Toxicological profile for polychlorinated biphenyls (PCBs)*, P.H.S. Department of Health and Human Services, Editor. 2000: Atlanta, GA.

10. Agarwal, S., S.R. Al-Abed, and D.D. Dionysiou, *A feasibility study on Pd/Mg application in historically contaminated sediments and PCB spiked substrates.* J. Hazard. Mater., 2009. **172**(2-3): p. 1156-1162.

11. Hopf, N.B., A.M. Ruder, and P. Succop, *Background levels of polychlorinated biphenyls in the U..S. population.* Sci. Total Environ., 2009. **407**(24): p. 6109-6119.

12. *The Toxic Stubstances Control Act (15 U.S.C. 2601-2692)*. 1976.

13. Jartun, M., et al., *Painted surfaces - Important sources of polychlorinated biphenyls (PCBs) contamination to the urban and marine environment.* Environ. Pollut. (Oxford, U. K.), 2008. **157**(1): p. 295-302.

14. Ruus, A., et al., *What caused the extreme PCB-concentrations in biota from the Sorfjord (western Norway) 2001-2002?* Organohalogen Compd., 2006. **68**: p. 2355-2357.

15. Kastanek, F. and P. Kastanek, *Combined decontamination processes for wastes containing PCBs.* J. Hazard. Mater., 2005. **117**(2-3): p. 185-205.

16. Kim, Y.-H. and E.R. Carraway, *Dechlorination of Pentachlorophenol by Zero Valent Iron and Modified Zero Valent Irons.* Environ. Sci. Technol., 2000. **34**(10): p. 2014-2017.

17. Gillham, R.W. and S.F. Ohannesin, *Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron.* Ground Water, 1994. **32**(6): p. 958-967.

18. Hughes, R., L. Gui, and R.W. Gillham, *Degradation of chlorinated butenes and butadienes in granular iron columns.* Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 2009. **44**(12): p. 1209-1218.

19. Sayles, G.D., et al., *DDT, DDD, and DDE dechlorination by zero-valent iron.* Environmental Science & Technology, 1997. **31**(12): p. 3448-3454.

20. Morales, J., R. Hutcheson, and I.F. Cheng, *Dechlorination of chlorinated phenols by catalyzed and uncatalyzed Fe(0) and Mg(0) particles.* J. Hazard. Mater., 2002. **90**(1): p. 97-108.

21. Quinn, J., et al., *Field Demonstration of DNAPL Dehalogenation Using Emulsified Zero-Valent Iron.* Environ. Sci. Technol., 2005. **39**(5): p. 1309-1318.

22. Agrawal, A. and P.G. Tratnyek, *Reduction of nitro aromatic compounds by zero-valent iron metal.* Environmental Science & Technology, 1996. **30**(1): p. 153-160.

23. Kanel, S.R., et al., *Transport of surface-modified iron nanoparticle in porous media and application to arsenic(III) remediation.* Journal of Nanoparticle Research, 2007. **9**(5): p. 725-735.

24. Kociolek-Balawejder, E. and L.J. Wilk, *A review of the methods for removing perchlorates from water.* Przemysl Chemiczny, 2009. **88**(11): p. 1221-1228.

25. Matheson, L.J. and P.G. Tratnyek,Processes, *Affecting Reductive Dechlorination of Cholrinated Solvents by Zero-Valent Iron.* Abstracts of Papers of the American Chemical Society, 1993. **205**: p. 91-ENVR.

26. Muftikian, R., et al., *X-ray Photoelectron Spectra of the Palladium-Iron Bimetallic Surface Used for the Rapid Dechlorination of Chlorinated Organic Environmental Contaminants.* Environ. Sci. Technol., 1996. **30**(12): p. 3593-3596.

27. Fournier, V., P. Marcus, and I. Olefjord, *Oxidation of magnesium.* Surface and Interface Analysis, 2002. **34**(1): p. 494-497.

28. Chuang, F.W. and R.A. Larson, *Zero-Valent Iron Promoted Dechlorination of Polychlorinated Biphenyls (PCBs).* Abstracts of Papers of the American Chemical Society, 1995. **209**: p. 233-ENVR.

29. Li, T. and J. Farrell, *Reductive dechlorination of trichloroethene and carbon tetrachloride using iron and palladized-iron cathodes.* Environmental Science & Technology, 2000. **34**(1): p. 173-179.

30. Lowry, G.V. and M. Reinhard, *Hydrodehalogenation of 1-to 3-carbon halogenated organic compounds in water using a palladium catalyst and hydrogen gas.* Environmental Science & Technology, 1999. **33**(11): p. 1905-1910.

31. Cheng, I.F., Q. Fernando, and N. Korte, *Electrochemical dechlorination of 4-chlorophenol to phenol.* Environmental Science & Technology, 1997. **31**(4): p. 1074-1078.

32. Patel, U.D. and S. Suresh, *Dechlorination of chlorophenols using magnesium-palladium bimetallic system.* J. Hazard. Mater., 2007. **147**(1-2): p. 431-438.

33. Kume, A., et al., *Pd/C-catalyzed practical degradation of PCBs at room temperature.* Applied Catalysis B-Environmental, 2008. **81**(3-4): p. 274-282.

34. Grittini, C., et al., *Rapid Dechlorination of Polychlorinated Biphenyls on the Surface of a Pd/Fe Bimetallic System.* Environ. Sci. Technol., 1995. **29**(11): p. 2898-900.

35. Kim, Y.-H., W.S. Shin, and S.-O. Ko, *Reductive Dechlorination of Chlorinated Biphenyls by Palladized Zero-Valent Metals.* J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng., 2004. **A39**(5): p. 1177-1188.

36. Liu, Y., et al., *Catalytic dechlorination of chlorophenols in water by palladium/iron.* Water Res, 2001. **35**(8): p. 1887-90.

37. Zhang, W.-x., C.-B. Wang, and H.-L. Lien, *Treatment of chlorinated organic contaminants with nanoscale bimetallic particles.* Catalysis Today, 1998. **40**(4): p. 387-395.

38. Zhang, W.X., *Nanoscale iron particles for environmental remediation: An overview.* Journal of Nanoparticle Research, 2003. **5**(3-4): p. 323-332.

39. Korte, N.E., et al., *The effect of solvent concentration on the use of palladized-iron for the step-wise dechlorination of polychlorinated biphenyls in soil extracts.* Waste Manage. (Oxford, U. K.), 2002. **22**(3): p. 343-349.

40. Suryanarayana, C., *Mechanical alloying and milling.* Progress in Materials Science, 2001. **46**(1-2): p. 1-184.

41. DeVor, R.W., *Determination of the Degradation Mechanism for Polychlorinated Biphenyl Congeners Using Mechanically Alloyed Magnesium/Palladium in Methanol*, in *Chemistry*. 2008, University of Central FLorida: Orlando, FL. p. 131.

42. Albo, R.L.F., et al., *Degradation of Triacetone Triperoxide (TATP) Using Mechanically Alloyed Mg/Pd.* Propellants Explosives Pyrotechnics. **35**(2): p. 100-104.

43. DeVor, R., et al., *Mechanism of the degradation of individual PCB congeners using mechanically alloyed Mg/Pd in methanol.* Chemosphere, 2009. **76**(6): p. 761-6.

44. Devor, R., et al., *Dechlorination comparison of mono-substituted PCBs with Mg/Pd in different solvent systems.* Chemosphere, 2008. **73**(6): p. 896-900.

45. Graham, L.J. and G. Jovanovic, *Dechlorination of p-chlorophenol on a Pd/Fe catalyst in a magnetically stabilized fluidized bed; implications for sludge and liquid remediation.* Chem. Eng. Sci., 1999. **54**(15-16): p. 3085-3093.

46. B. Aitken, C.G., C. Clausen, J. Quinn. *Variables Associated With Mechanical Alloying of Bimetals for PCB Remediation*. in *5th Annual International Conference on Remediation of Chlorinated and Recalcitrant Compounds*. 2006. Monterey, CA.

47. *Method 3550C Ultrasonic Extraction*, in *Test Methods for Evaluating Solid Waste (SW-846)*. 2007, Environmental Protection Agency.

48. *Method 3665A Sulfuric Acid/Permanganate Cleaup*, in *Test Methods for Evaluating Solid Waste (SW-846)*. 1996, Environmental Protection Agency.

49. *Method 8082A Polychlorinated Biphenyls (PCBs) By Gas Chromatography*, in *Test Methods for Evaluating Solid Waste (SW-846)*. 2007, Environmental Protection Agency (EPA).

50. Hadnagy, E., L.M. Rauch, and K.H. Gardner, *Dechlorination of polychlorinated biphenyls, naphthalenes and dibenzo-p-dioxins by magnesium/palladium bimetallic particles.* J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng., 2007. **42**(6): p. 685-695.

51. Choi, H. and S.R. Al-Abed, *Effect of reaction environments on the reactivity of PCB (2-chlorobiphenyl) over activated carbon impregnated with palladized iron.* J. Hazard. Mater. **179**(1-3): p. 869-874.

52. DeVor, R.C.-K., Kathy; Aitken, Brian; Maloney, Phillip; Holland, Erin; Talalaj, Lukasz; Elsheimer, Seth; Clausen, Christian A.; Geiger, Cherie L, *Mechanism of the degradation of individual PCB congeners using mechanically alloyed Mg/Pd in methanol.* Chemosphere, 2009(76): p. 761-766.